EFFECT OF A CO-SOLVENT FEEDSTOCK ON THE SYNTHESIS OF BIODIESEL VIA HETEROGENEOUS CATALYSIS

By

Matthew Jon Littell

Frank Jones
Professor of Engineering
Committee Chair

Tricia A. Thomas
Assistant Professor of Engineering
Committee Member

Bryan J. Ennis
Associate Professor of Engineering
Committee Member

EFFECT OF A CO-SOLVENT FEEDSTOCK ON THE SYNTHESIS OF BIODIESEL VIA HETEROGENEOUS CATALYSIS

By

Matthew Jon Littell

A Thesis Submitted to the Faculty of the University of Tennessee at Chattanooga in Partial Fulfillment of the Requirements of the Degree of Master of Science: Engineering

The University of Tennessee at Chattanooga

Chattanooga, Tennessee

May, 2015

ABSTRACT

Research has been conducted regarding a single phase feedstock solution to produce biodiesel. Biodiesel production usually uses a two-phase feedstock which causes several issues. The two different feed stocks have been compared using several methods. The single phase feedstock, consisting of soybean oil, free fatty acid, and methanol in a 1:1:1 volume ratio has proven to be successful in all areas of study with the heterogeneous catalyst nickel oxide.

Microreactors are being used to improve the efficiency of the production of biodiesel. The smaller scale makes it possible to produce biodiesel in seconds compared to what industrial biodiesel production requires hours to accomplish. There are improvements than can be made to the next generation of microreactors to increase the efficiency.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

FAME, Fatty Acid Methyl Ester

FAEE, Fatty Acid Ethyl Ester

NREL, National Renewal Energy Laboratory

CO_2, Carbon Dioxide

FEP, Fluorinated Ethylene-Propylene

WCO, Waste Cooking Oil

PTFE, Polytetrafluoroethylene

KOH, Potassium Hydroxide

NaOH, Sodium Hydroxide

FFA, Free Fatty Acid

MeOH, Methanol

SBO, Soybean Oil

HPLC, High Pressure Liquid Chromatography

H_2SO_4, Sulfuric Acid

ID, Inner Diameter

C, Celsius

CaO, Calcium Oxide

UTC, University of Tennessee at Chattanooga

NiO, Nickel Oxide

RBF, Round Bottom Flask

RPM, Revolutions per Minute

GC, Gas Chromatography

FID, Flame Ionization Detector

CBG, Combined Bound Glycerin

MSTFA, n-methyl-n-(trimethylsilyl) trifluoroacetamide

MW, Molecular Weight

cp, Centipoise

g, Grams

mL, Milliliters

Re, Reynold's Number

NMR, Nuclear Magnetic Resonance

SSV, Stainless Steel Vial

LIST OF SYMBOLS

μ, Viscosity

r, Density

CHAPTER 1

INTRODUCTION

The world is in constant demand for fuels and relies heavily on fossil-based fuels. However, there is a growing concern that burning the fossil-based fuels contributes to global warming due to carbon emissions.[1] To address this concern, research into biofuels is being conducted. Biofuels are fuels that are derived from renewable resources. One type of biofuel is biodiesel.

Biodiesel is biodegradable, non-flammable, non-toxic, and has a favorable combustion-emission profile. It produces less carbon-monoxide, sulfur dioxide and unburned hydrocarbons compared to petroleum based diesel.[2]. The current process in industry involves agitating a methanol-oil mix in a large batch reactor for an hour while heating and reacting. Then the mixture must sit for several hours to cool. Finally, the catalyst must be neutralized and the byproduct, glycerol, must be separated from biodiesel.[3] The entire batch process takes several hours to complete.

Dr. Frank Jones' research group is focused on finding better, more efficient ways to produce biodiesel. By improving the efficiency of production more biodiesel could be produced and help relieve the dependency on fossil based fuels. The research group has focused on micro-scale production. This has been shown to reduce processing time significantly compared to the current industrial processes. Previous work has been completed by the research group. Jennifer

Lewis (UTC DHON ’10) simulated microreactors for biodiesel production.[4] The optimal channel dimensions were found in this study. Experimental work was done by Trip Dacus (UTC DHON ’10), determined promising heterogeneous catalysts to further speed up the reaction.[5] Eric Snider, (UTC DHON ’12), studied the behavior of microreactors and compared their processing time compared to stirred tank reactors in the production of biodiesel.[6] Ben Kegley determined the optimal miscibility of a free fatty acid as a co-solvent.[7] The research group continually makes technological advancements on this process. The goal of this thesis is to compare a single phase feedstock compared to a two-phase feedstock.

CHAPTER 2

BACKGROUND INFORMATION

This section gives an in depth background of the research concerning biodiesel. It is important to discuss what biodiesel is and why research of it is important. Previously published research is looked at to determine the best route to proceed with the research.

2.1 Biodiesel Chemistry

The chemical structure of biodiesel is considered a fatty acid methyl ester or FAME. This molecule is can be derived from vegetable oils and animal fats. The 18 carbon FAME molecule is show in Figure 1.

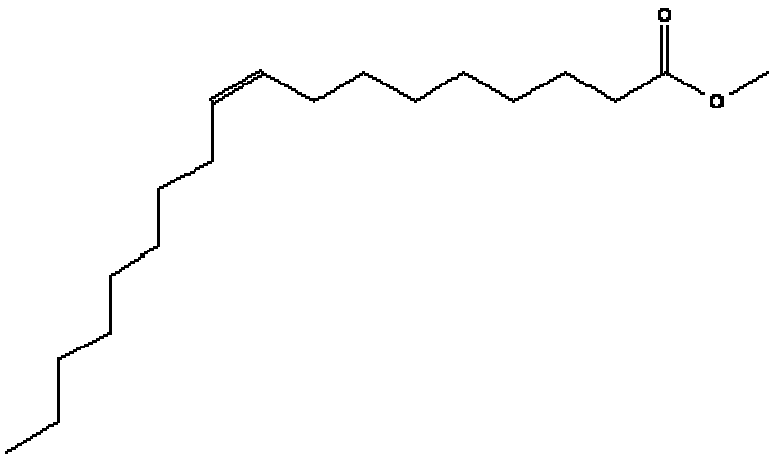

Figure 1 18 Carbon FAME Molecule[8]

Biodiesel is different from the petroleum diesel molecule because of the ester functional group. The diesel molecules lack the ester group. Figure 2 shows a typical diesel molecule.

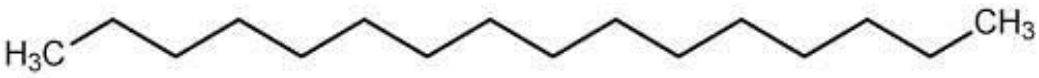

Figure 2 Petroleum Derived Diesel Molecule[9]

These two molecules, biodiesel and diesel, have slightly different properties when examining the carbon cycle. In combustion, CO_2 is a product because of oxygen reacting with carbon. In order to compare the two molecules, diesel is used as a reference point, as it is more widely used in the world. Diesel, when it burns, increases the amount of CO_2 in the atmosphere, because it is derived from fossils—a substance that does not consume CO_2. However, combusting biodiesel is considered to be CO_2 neutral, because biodiesel is derived from biomass. Biomass, when alive, consumes CO_2 so the overall carbon increase is considered significantly less. To illustrate the effect biodiesel has on emissions the National Renewable Energy Laboratory (NREL) performed an experiment to test the CO_2 emissions compared to petroleum diesel.[10] In the experiment the percent of the percentage of biodiesel was varied in the feedstock. The results are show when using only biodiesel the emissions can be reduced by nearly 80%, see Figure 3. This means that the more biodiesel that is used the less carbon is released into the atmosphere by a significant amount.

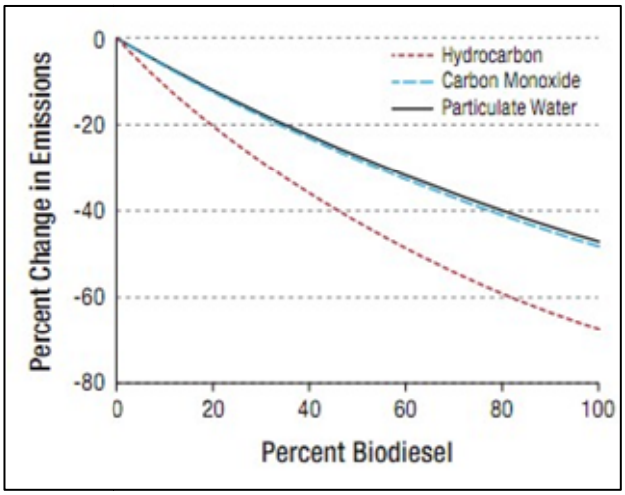

Figure 3 Emissions data for biodiesel[10]

The process to obtain a biodiesel molecule requires a chemical reaction known as transesterification, seen in Figure 4. A triglyceride molecule reacts with three alcohol molecules to produce glycerol and three molecules of biodiesel. There are two common alcohols that are used, they are methanol and ethanol. If methanol is used then the product will be fatty acid methyl ester (FAME), likewise if ethanol is used the product will be fatty acid ethyl ester (FAEE).

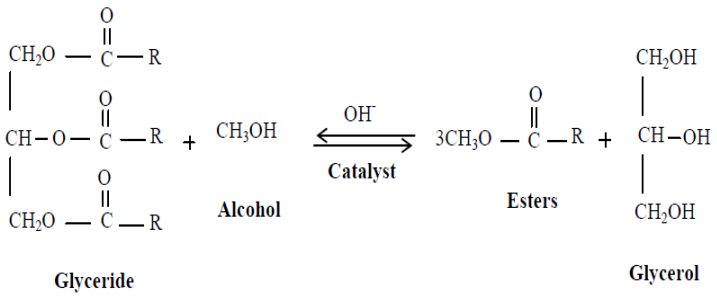

Figure 4 Transesterification Reaction with a Triglyceride[11]

Figure 4 shows the net reaction to obtain three fatty acid ester molecules, which is the ideal end product. The process involves three individual reactions, each of which are transesterification reactions. In each step, the ester group is cleaved from the glyceride molecule and the alcohol retains the ester. The reaction requires a catalyst—a substance that increases the rate of a chemical reaction without itself undergoing any permanent changes.[12] This forms two intermediates: di-glyceride and mono-glyceride molecules. After the third transesterification reaction the glycerol molecule is formed. This process is depicted in Figure 5. The detailed acid and base catalyzed mechanisms will be discussed in a later section 3.5.1.

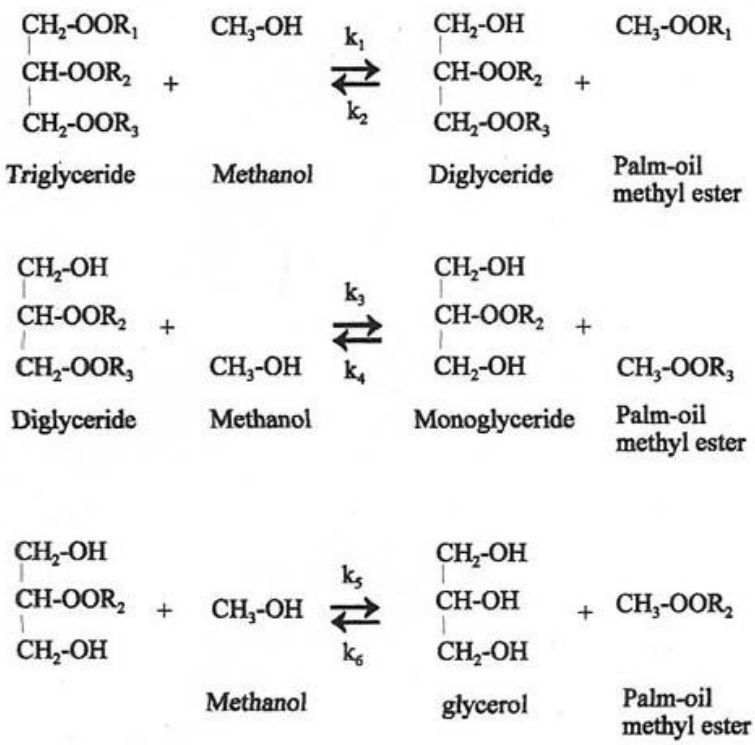

Figure 5 Reaction Scheme to Produce Three Biodiesel Molecules

2.2 Various Microreactors for biodiesel synthesis

Microreactors are studied because the process of using microreactors is less costly due to reduced equipment size and lower reactant consumption.[13] Microreactors can be classified in three main categories: microtube, capillary, and microchannel. They differ in geometry and material. This section will examine each type of microreactor.

2.2.1 Microtube Reactors

Microtube reactors use a cylindrical system. The tube diameters are in the range from micrometers to millimeters. Due to the nature of this system there are high heat to mass transfer rates with a short diffusion distance, which results in great performance in liquid-liquid phase reactions. This system shows a higher conversion result in a shorter time compared to batch reactors.[2]

2.2.1.1 Biodiesel Production Using Sunflower Oil

Guan et al. used sunflower oil with methanol in a microtube reactor.[14] The experimental setup is seen in Figure 6. The microtube used in this experiment was a transparent fluorinated ethylene-propylene (FEP) tube with an inner diameter of 0.8 mm and 0.3 m long. The tube was placed in a constant temperature oil bath at the required temperature. Methanol, which had 4.5 wt% KOH premixed, and sunflower oil were fed separately by two syringe pumps—1&2. These syringe pumps fed into a T-connector, which aids in the mixing process, therefore, it is called a T-mixer. The T-mixer feeds into the microtube. The molar ratio of sunflower oil to methanol was kept constant at 1:24, which is a 1:1 volume ratio. The reaction temperature was 60ºC, with a

flow rate of 8.2 cm^3/h. It was observed at the entrance region of the microtube the oil and methanol traveled as segmented two-phase flow. As the reaction progressed the segmented two-phase flow became a quasi-homogenous phase. This was due to the accumulation of fine droplets due to reaction completion. The products were collected in a glass bottle and the reaction was terminated by the addition of acetic acid through a syringe pump—3. After 100 seconds, when the flow became quasi-homogenous, the yield of FAME was 100%.

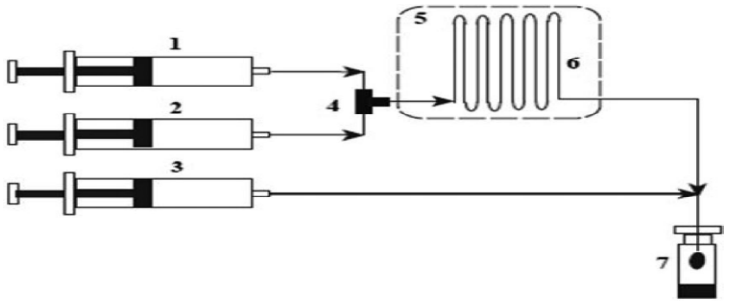

Figure 6 1 and 2) Syringe pumps for methanol and sunflower oil, 3)Syringe pump for acetic acid, 4) T-Mixer, 5) Oil bath, 6) FEP microtubule reactor, 7) Collection bottle[14]

2.2.1.2 Flow behavior in microtube reactors using waste cooking oil

Teshima et al. used waste cooking oil (WCO) and sunflower oil to produce biodiesel as well as examine the flow behavior.[15] Transparent polytetrafluoroethylene (PTFE) tubes with diameters of 0.46, 0.68, 0.86, and 0.96 mm were used as microtube reactors and allowed for observations of fluid flow behavior. The reactor set up is the same as Figure 6.

To better visualize the flow, the methanol solution was dyed with inert red phloxine B. Red phloxine B is soluble in glycerol but not the oil. Thus, the liquid in the microtube was presented as a red liquid and a colorless liquid. Syringe pumps were used to provide a steady flow rate to provide a residence time of 252 s. The temperature was kept at 40 or 60ºC. Pictures

were taken with an optical microscope equipped with a digital camera or just the digital camera, where appropriate.

Figure 7 is a visualization of the experimental microreactors with the methanol/KOH-oil liquids passing through them. Each of the pictures illustrates a different microtube diameter. When the liquid-liquid system first enters into the tubes it appears as individual droplets. But as the fluid continues through the microtube the droplets appear smaller till there only a red solution exists, which is indicative of the transesterification reaction having taken place in substantial amounts. From this it is determined that with a smaller diameter a higher yield will result. The smaller diameter will also assist with better heat transfer to the fluids.

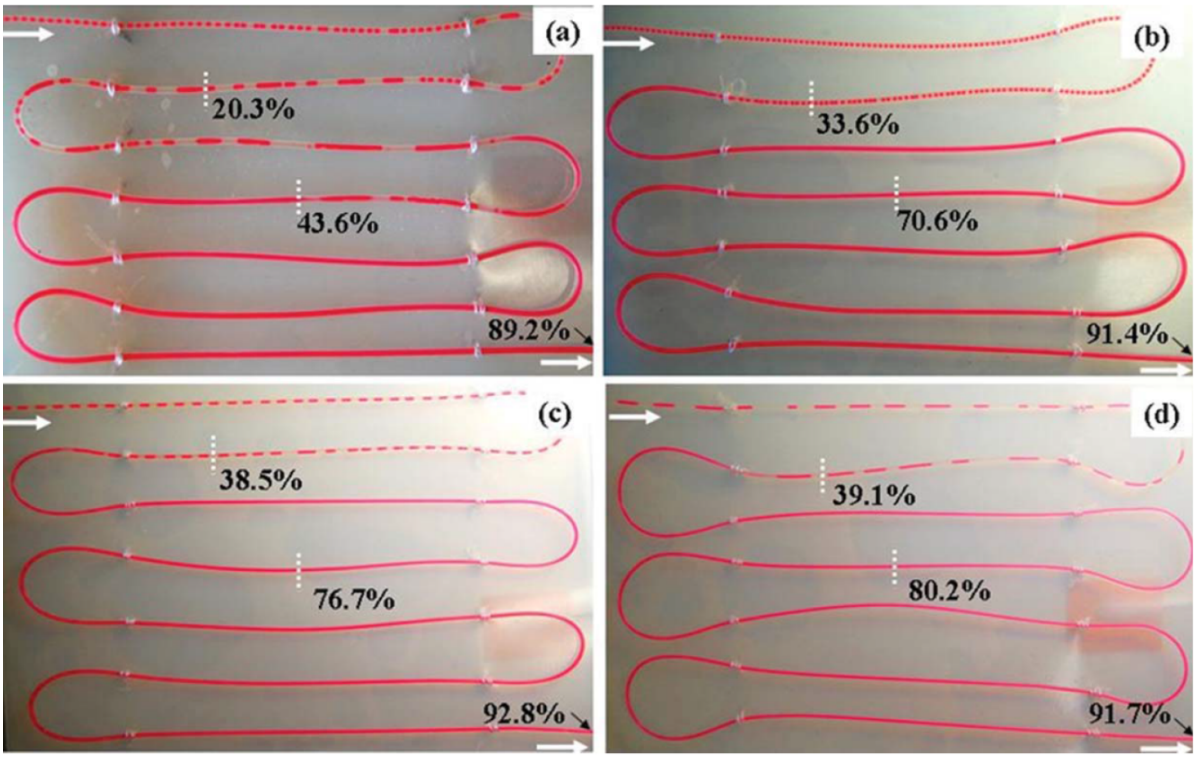

Figure 7 Visualization of flow patterns using WCO for the production of FAME using different diameters: a) 0.96 mm b) 0.86 mm, c) 0.68 mm, d) 0.46 mm[15]

2.2.1.3 Biodiesel production using waste cooking oil (WCO)

Tanawannpong et al. used waste cooking oil in a microtube reactor to produce biodiesel.[2] The reaction took place in two steps, because a free fatty acid (FFA) content higher than 0.5 wt% in the WCO. The catalysts NaOH or KOH are limited only to oils that contain less than 0.5 wt% FFA. The first step involves lowering the acid value of the WCO by an esterification reaction. The second step then uses the products to produce biodiesel by a transesterification reaction in the microtube reactor. Both steps use the same experimental set up, with different reactants. See Figure 8 for the experimental set up.

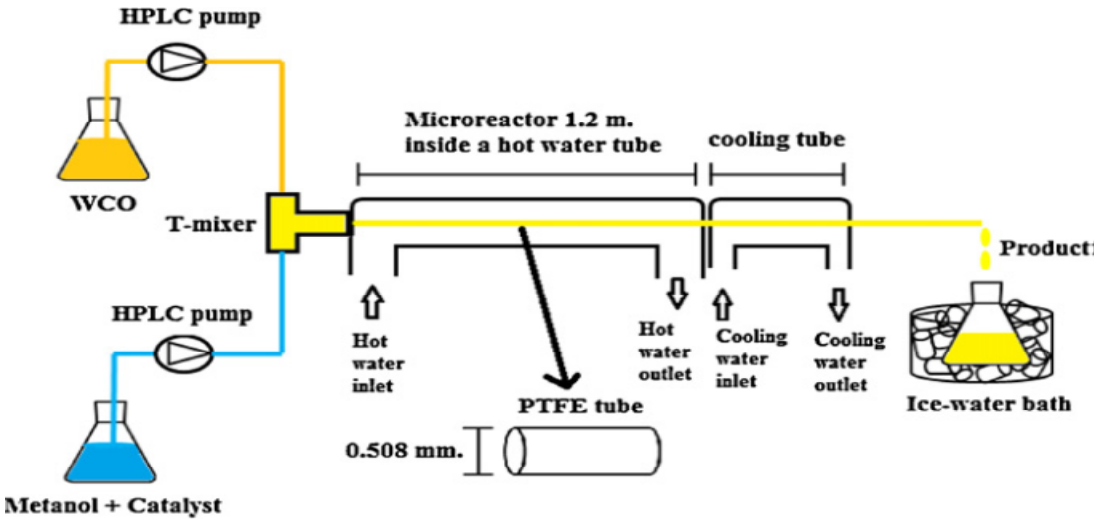

Figure 8 Experimental setup for microtube reactor—Two step process[2]

The microtube was made of polytetrafluoroethylene (PTFE) with an inner diameter of 0.508 mm and a length of 1.2 m. This microtube was placed in a hot water jacket in order to control the reaction temperature. At the entrance, a T-mixer was used to connect the WCO and the methanol—mixed with the catalyst. The reactants were pumped via a HPLC pump. At the exit the microtube was placed in a cold water jacket to terminate the reaction. Then finally, the product collection flask was placed in an ice bath.

The optimal conditions were determined for the acid-catalyzed pretreatment step to have a molar ratio of methanol-to-oil ratio of 9:1, a 1 wt% sulfuric acid, a reaction time of 5 seconds, and a reaction temperature of 65ºC. The products collected appeared in two phases, methanol at the top and oil at the bottom. The oil was then washed with deionized water and dried at 107ºC

for 30 minutes. After the esterification reaction, the WCO product had an acid value of 0.89 mg KOH/g compared the value at the starting point of 3.96 mg KOH/g. This is an acceptable amount to use KOH as the catalyst for the transesterification process. The difference between the esterification and transesterification reactions can be seen in section 3.5.1.

For the transesterification reaction the optimal condition are the same as for the esterification reaction, except 1 wt% KOH is now used instead of the H_2SO_4. The process remained the same. This resulted in a methyl ester yield of 91.76%.

2.2.2 Capillary Microreactors

The difference between a microtube reactor and capillary reactor is the type of material the tube is made of and the length of the tube. Capillary microreactors are made out of either quartz or stainless steel. They will have an inner diameter (ID) of either 0.25 mm or 0.53 mm with a length of 30 m. The inlet side of this reactor is connected to a high performance liquid chromatography (HPLC) with the outlet connected to a collection vial. This microreactor is kept immersed in a water bath to maintain the temperature during the experiment.[16]

Sun et al. used unrefined rapeseed oil and cottonseed oil with methanol and KOH as a catalyst to produce biodiesel.[16] A mixture of oil, methanol, and KOH was prepared before entering the microreactor, by vigorous stirring. The mixture was then injected into the microreactor at a constant flow rate and temperature. The products appeared in three phases: the top was methanol, the middle was methyl ester, and the bottom was glycerol. The methanol was evaporated off and the methyl ester phase was removed and washed with DI water. Three experiments were conducted to find the optimal conditions for methyl ester yields.

The first experiment used rapeseed oil in a quartz capillary with an ID of 0.53 mm. The optimal conditions for methyl ester yield were determined to be when the molar ratio of oil to methanol was 1:6 with 1 wt% KOH, a temperature of 60ºC, and a residence time of 8.2 minutes. This resulted in a methyl ester yield of 96.7%.

The second experiment used rapeseed oil in a quartz capillary with an ID of 0.25 mm. The optimal conditions for methyl ester yield were determined to be when the molar ratio of oil to methanol was 1:6 with 1 wt% KOH, a temperature of 60ºC, and a residence time of 6 minutes. This resulted in a methyl ester yield of 98.8%. It was found that the smaller diameter capillary tube resulted in a higher yield with a lower residence time.

The third experiment was performed to investigate the transesterification reaction using microchannels. The experiments used cottonseed oil and a microchannel reactor assembled by two parallel stainless steel capillary tubes with an ID of 0.25 mm.[16] The optimal condition for methyl ester yield was determined to be when the molar ratio of oil to methanol was 1:6, with 1 wt% KOH, a temperature of 60ºC, and a residence time of 6 minutes. The methyl ester yield was found to be 95%. The experiment concluded that microchannel reactors can be used in the synthesis of biodiesel. However, the reactants were premixed, so the benefits of this kind of microreactor have to still be determined.[16]

These results are similar to the microtube reactors with respect to percent yield. However, the residence time is significantly longer. The microtube reactors had optimal residence times of

several seconds; the capillary reactors had residence times in the minutes. The shorter residence time is better for production of biodiesel.

2.2.3 Microchannel Reactors

The difference between microtube and microchannel reactors is the geometry of the area where the solution is flowing. A microtube has a cylindrical geometry while a microchannel has a rectangular geometry with respect to the channels.

2.2.3.1 Slit-Channel Reactors

Kalu et al. used four slit-channel reactors to synthesize biodiesel.[17] The four slit-channel reactors all had a channel width of 2 mm and a channel length of 15.24 cm. Each had a different depth: 1 mm, 2 mm, 5 mm and 10 mm. They were made by using two parallel plastic blocks made of nylon on bottom and polycarbonate on top, see Figure 9. The nylon block had the channel drilled into it, while the polycarbonate block was attached to the nylon black for visualization purposes. A neoprene gasket was used to seal the two pieces together and stop leakage.

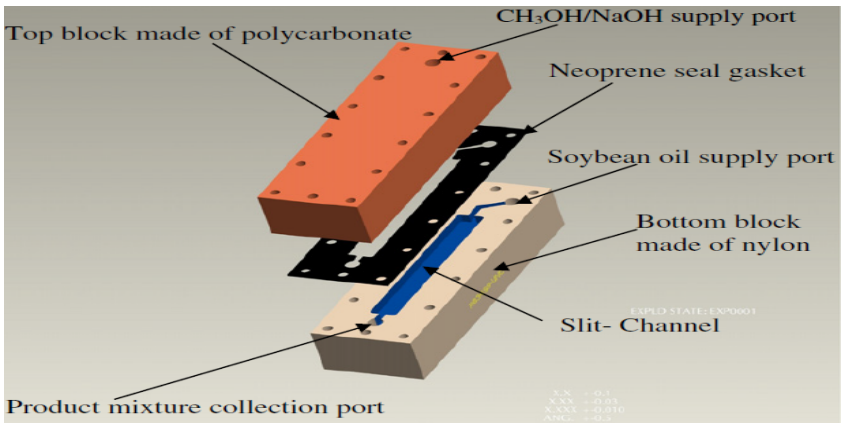

Figure 9 Slit-channel reactor [18]

The experiment used soybean oil, methanol, and NaOH as the catalyst. Pulsatron pumps were used to feed the reactants into the microchannel via a T-mixer. Methanol and NaOH mixture—0.0263g NaOH per 1 mL methanol—were fed through the polycarbonate block with the oil through the nylon block. The molar ratio of SBO to methanol was 1:6; the reaction temperature was conducted in a range from 55-65ºC. The temperature was maintained by a

shaker bath. The products where fed in to a container placed in an ice bath to terminate the reaction. It was determined that the yield of FAME is a function of channel depth and residence time. As channel depth decreases along with residence time the biodiesel yield increases. No quantitative results were published.

2.2.3.2 Zigzag microchannel reactors

Wen et al. used microchannels on a steel plate to produce biodiesel.[19] These channels are made of stainless steel (SS316L). The channel was created in the steel by using an electric spark process. The channels are rectangular in shape with a total length in the steel of 1.07 m. The reactor has three main parts, as seen in Figure 10. The top sheet has inlet and outlet holes. The middle sheet has wells for the inlet and outlet along with the channels. The bottom sheet is for stability of the entire reactor.

To assemble the reactor the three sheets are polished to a roughness of 2 µm, followed by a cleaning with acetone. A diffusion bonding process is then carried out at 1000ºC, at 10 MPa of pressure, and in a vacuum for three hours. After this process the reactor is cooled to room temperature. Two ferrule fittings are then bonded on the outlet and inlet of the cover sheet for plumbing.[19]

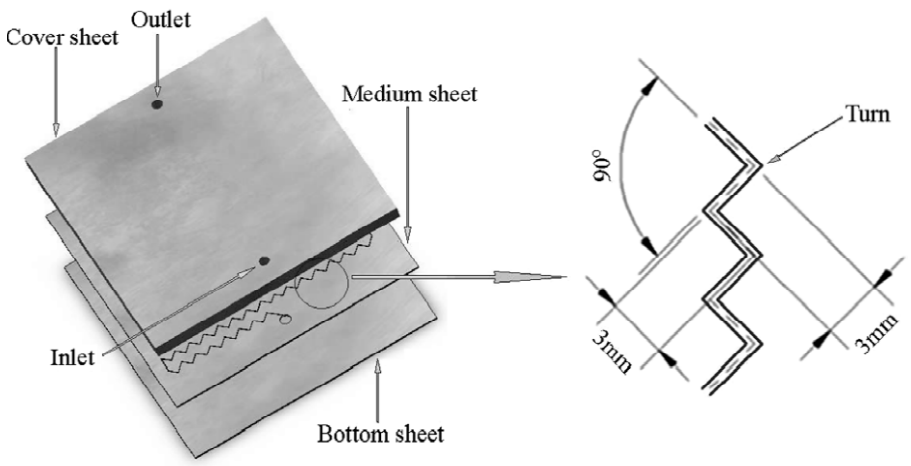

Figure 10 Configuration of the zigzag microchannel reactor [20]

The production of biodiesel used soybean oil, methanol, and NaOH as a catalyst in nine different reactors, named Zigzag-1 through Zigzag-9. The hydraulic diameters of the channels ranged from 240 µm to 900 µm. Methanol with 1.2 wt% NaOH dissolved and SBO were injected using two syringe pumps. The molar ratio of oil to methanol was 1:9 and the reaction temperature was kept at 56ºC by a water bath. There was a T-connector before the inlet of the microchannel. The collection flask was placed in an ice bath to terminate the reaction. The collection was centrifuged at 8000 rpm for 10 minutes. This facilitated the separation of phases. The methanol was then evaporated off.

From the experiments, it was determined the methyl ester yield increased as the number of turns increases and as channel sized decreased. With a residence time of 28 seconds using the smallest channel and most turns, methyl ester content was found to be 99.5%. See Table 1 for full results.

Table 1 Zigzag Type Reactors[19]

Name	Section (μm x μm)	Hydraulic diameter (μm)	Turns	Yield* (%)
Zigzag-1	200 x 300	240	350	97.3
Zigzag-2	300 x 500	375	350	91.3
Zigzag-3	500 x 500	500	350	81.1
Zigzag-4	500 x 900	643	350	80.9
Zigzag-5	900 x 900	900	350	77.8
Zigzag-6	500 x 500	500	10	60.0
Zigzag-7	500 x 500	500	50	63.2
Zigzag-8	500 x 500	500	100	70.2
Zigzag-9	500 x 500	500	200	79.8

2.3 Factors for Biodiesel Synthesis

There are several factors that influence biodiesel synthesis. This section will look at the factors of temperature, channel size, and residence time.

2.3.1 Reaction Temperature

Reaction temperature plays a major role in reaction characteristics. As temperature is increased the more kinetic energy there is in the molecules resulting in molecules colliding into each other more frequently than compared to cooler temperatures. Diffusion is also based on the kinetic energy of the molecules. Higher temperature means quicker diffusion times. Solvation is

also dependent on temperature. The high temperatures will result in more molecules being solvated. Thus, the molecules will have a more favorable interaction. This will also decrease the needed residence time to reach the optimal yield. These ideas are useful for both homozygous and heterozygous catalysis.

Guan et al. conducted a good experiment to compare reaction temperature to oil conversion.[14] The experiments were conducted using three different molar ratios of oil to methanol: 1:4.6, 1:11.3, and 1:23.9. The residence time was kept constant at 56 seconds and the same stainless steel microtube reactor was used—ID of 0.8 mm and a length of 500 mm. See Figure 11 for the graphical comparison. As the temperature increase the conversion of oil was increased near linearly. This is contributed to better miscibility due to the increase of temperature.

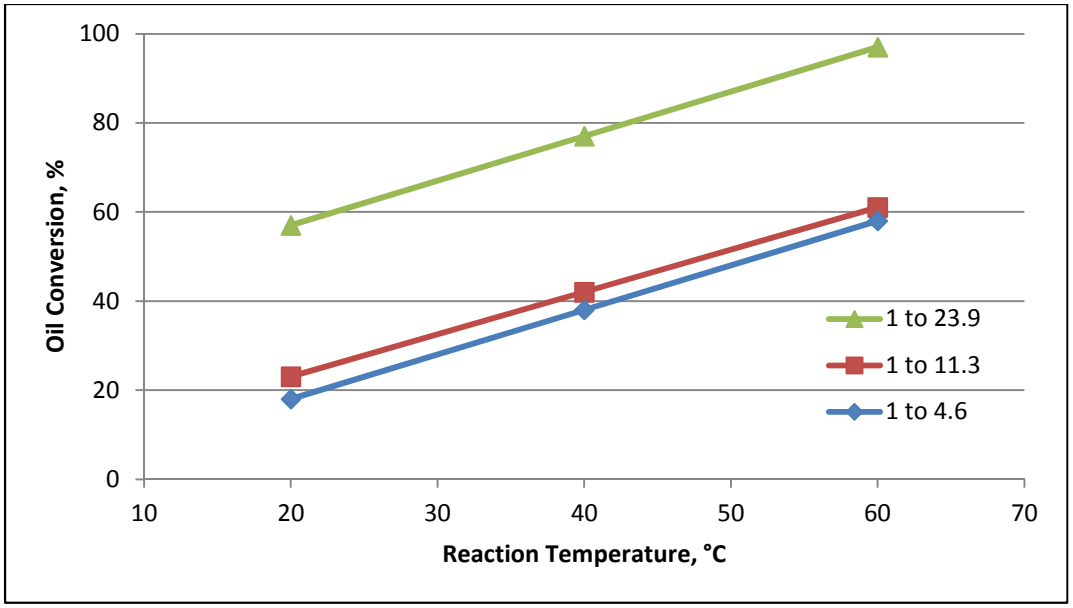

Figure 11 Oil conversion as a function of temperature. Oil to methanol ratios of 1:23.9, 1:11.3, and 1:4.6[14]

Sun et al. increased the reaction temperature above the boiling point of methanol (65.7°C), which was used in the transesterification reaction.[16] The conclusion of having a temperature hotter than the boiling point was a reduction in methyl ester yield. At 60°C the methyl ester yield was 99.4% and at 70°C the yield was 99.1%. This is only a slight decrease; however this decrease can be attributed to the flow changing from a liquid-liquid to a liquid-gas flow. The changing of methanol to a gas will decrease the available methanol that can be solubilized and react. This also increases the rate of saponification of the glycerides by the alkaline catalyst.[16]

2.3.2 Microchannel Size

Guan et al. conducted an experiment that compares the ID of microtube reactors to oil conversion.[14] In the experiment, the temperature was kept constant at 60°C. There were three different methanol to oil molar ratios compared: 4.6, 11.3, and 23.9. Four microtube reactors were used with lengths and IDs of 1000 mm for 0.4 mm ID, 444 mm for 0.6 mm ID, 250 mm for 0.8 mm ID, and 160mm for 1.0 mm ID. The lengths were changed in order to keep the same residence time, 26 seconds, and volumetric flow rate. Figure 12 summarizes the findings of the experiment. As the microtube ID decreased the velocity of the fluid was increased to maintain the flow rate.

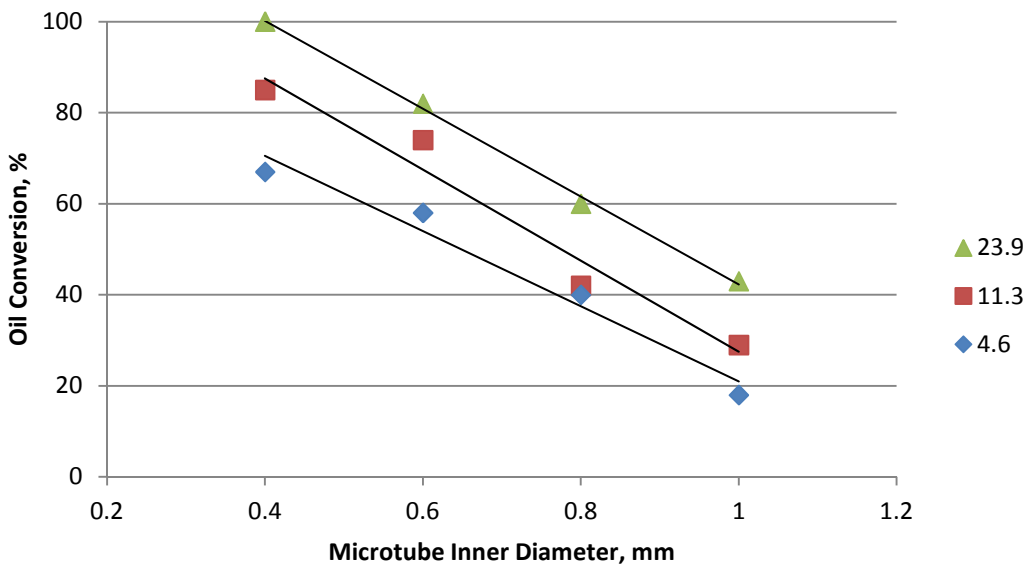

Figure 12 Oil conversion as a function of microtube reactor inner diameter, mm. Oil to methanol molar ratios are 23.9, 11.3, 4.6.[14]

Wen et al. examined the effect of channel size by using the zigzag type of microchannel reactor.[19] Nine different types of reactors were compared. Table 1 summarizes the types of reactors. Examining Zigzag-1 through Zigzag-5 gives the best comparison of microreactor channel size effects since the number of turns is kept constant. As the hydraulic diameter decreases the yield increases.

Since methanol and soybean oil are immiscible, droplet size was examined. It was determined that yield is highly dependent on droplet size. During this experiment a laser scattering method and optical microscope were used to determine droplet size. Figure 13 shows the droplet distribution in Zigzag-1 and Zigzag-3. As the droplet size decreases there is more surface area for the oil and methanol to interact and react. Therefore, the smaller reactor channels give smaller droplet size and larger surface interactions, thus better yield.

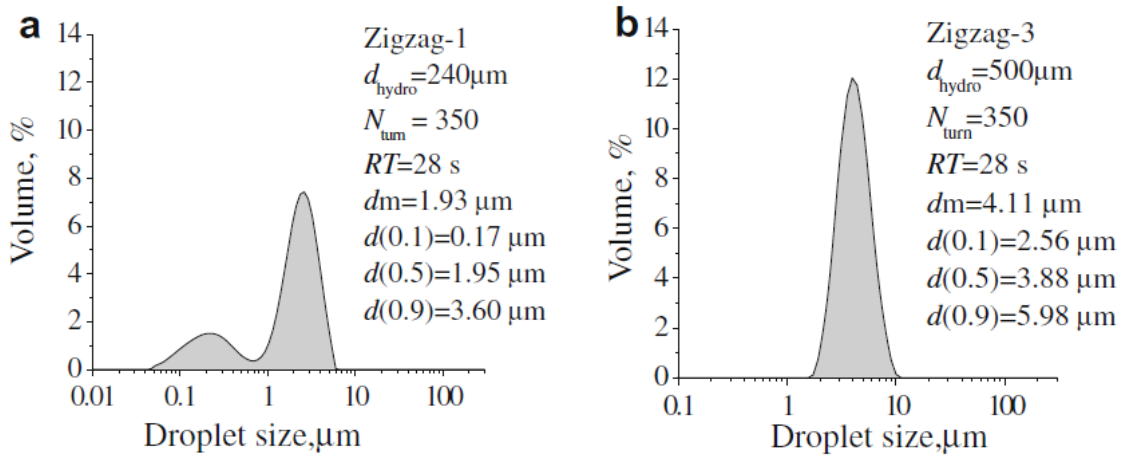

Figure 13 Droplet size distribution of Zigzag-1 and Zigzag-3 with oil to methanol molar ratio of 1:6 and reaction temperature of 60°C[19]

2.3.3 Residence Time

Residence times in microreactors are 10-100 times shorter compared to those of conventional batch reactors which is an advantage of microreactors.[21] Guan et al. was able to achieve 100% oil conversion in less than 100 seconds in a microtube reactor using sunflower oil and methanol and KOH as the catalyst, and 98% conversion in 60 seconds with a methanol to oil molar ratio of 1: 23.9.[14] Using waste cooking oil, in an esterification and transesterification

reaction it was noted that increasing the residence time increased the acid value. So a minimum acid value was found with a residence time of five seconds which then gave a FAME yield of 91.76%.[2] In capillary microreactors the yield increased as the residence time increased, to an extent. The maximum methyl ester yield of 99.4% was found at a residence time of six minutes.[16] An increase past six minutes decreased the methyl ester yield due to the equilibrium nature of the transesterification reaction. Guan conducted several experiment to test the effect of residence time to oil conversion. Figure 14 is with three different methanol to oil molar ratios—4.6, 11.3, and 23.9. The temperature was kept at 20°C. This experiment showed at higher residence times there was a limit to the conversion. The limit was varied with the molar ratio; as the molar ratio was higher so was the conversion limit.

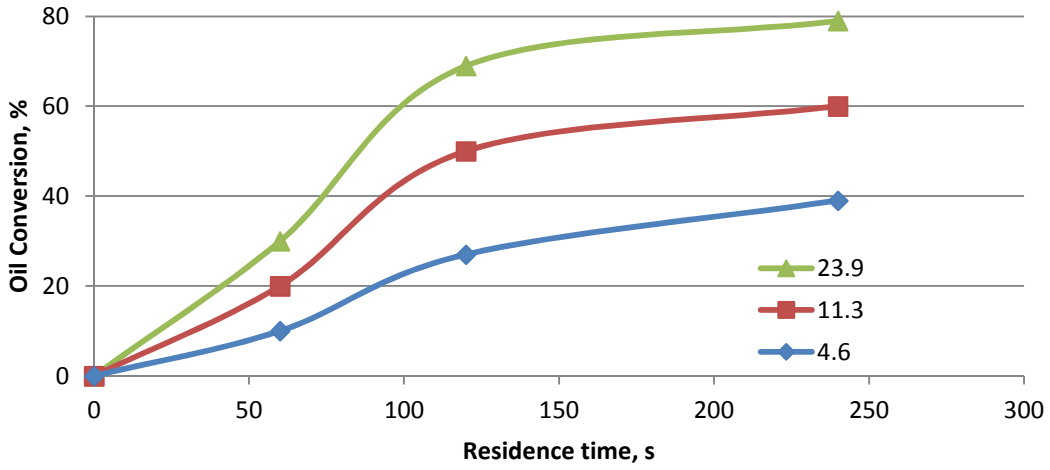

Figure 14 Oil conversion as a function of residence time, with methanol to oil molar ratios of 23.9, 11.3, and 4.6.[14]

2.4 Mixing

There are several ways to mix solutions together. This section discusses a few of the possibilities: diffusion, zigzag geometry, and ultrasonic.

2.4.1 Diffusion

Diffusion is the process of one type of molecule migrating through a solution of another type. This is based on the kinetic energy, solubility, and concentration of the molecules. As the length the molecules have to travel gets smaller the diffusion time gets smaller, Equation 1.

$$t_D = \frac{L^2}{D} \tag{1}$$

In Equation 1, t_D represents the time it takes for an individual particle to diffuse through the liquid, L is the length the particle must travel, and D is a diffusion coefficient. The smaller the system the less time it takes for a molecule to diffuse. This helps to explain why the smaller microreactors have better yields at a given residence time.

2.4.2 Zigzag Geometry

Wen et al. uses zigzag geometry as a static mixing mechanism.[19] There were nine microchannel reactors made. Table 1 gives the specifications of each reactor made. By comparing reactors named Zigzag-3, 7-8 on Table 1 the mixing effects can be examined. As the number of turns increases the yield also increases. This is evidence that zigzag geometry works as a mixing mechanism.

2.4.3 Ultrasonic

Ultrasonic mixing was shown to be an effective method of mixing in microchannels.[22] Ultrasound waves alternately compress and stretch the molecular spacing of the medium through which it passes. This can cause cavitation to occur. When the cavity collapses energy is generated for chemical and mechanical effects. This causes mass transfer though the fluids. Thus, mixing occurs

The effects of the ultrasonic mixing were found to have a conversion to FAME near 96% with a residence time of two minutes. A FAME yield of100% was obtained at 45 min at 60ºC with a methanol to oil molar ratio of 4.5:1.

2.5 Catalysts for Biodiesel Production

The reactions used to produce biodiesel require a catalyst in most cases. There are two reactions esterification and transesterification. Several catalysts can be used for these reactions which can be broken into two groups: homogenous and heterogeneous. Homogenous catalysts are a liquid and mix in with the alcohol phase. Heterogeneous catalysts are solid that do not dissolve with the reactants.

2.5.1 Homogeneous

A homogeneous catalyst will be dissolved in the alcohol phase of the reactants. These catalysts can be either a strong acid or a strong base. The most common acids used are sulfuric acid and hydrochloric acid; and the most common bases used are NaOH and KOH. The mechanisms for the production of biodiesel differ for a base and acid.

2.5.1.1 Acid

When an acid is used there are several steps, outlined in Figure 15. 1) There is a proton transfer from the acid catalyst to the carbonyl oxygen. This increases the electrophilicity of the carbonyl carbon. 2) The carbonyl carbon is then attacked by the nucleophilic oxygen atom of the alcohol. 3) Tautomerism, the migration of a proton. 4) The loss of water with this oxonium ion and subsequent deprotonation gives the ester.

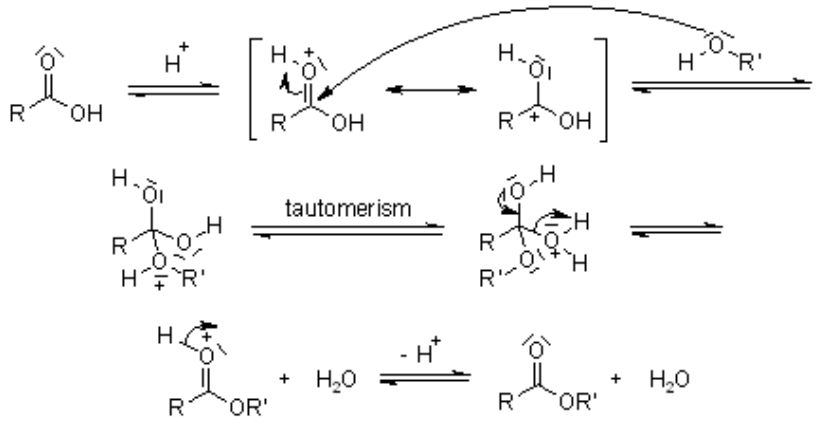

Figure 15 Acid catalyzed esterification mechanism[23]

Tanawannapong et al. used sulfuric acid as a catalyst in order to reduce the acid value of the WCO.[2] The first step of the process was an esterification reaction with the free fatty acid. The acid number must be less than 1 mg KOH/g in order to use KOH to catalyze the transesterification reaction of the WCO, specifically the triglycerides. The process was successful and reached at 91.76% yield. Sun et al. also used this two-step process.[16] The highest yield of FAME was achieved when transesterification of cottonseed oil with methanol at 120ºC

with a residence time of 20 minutes. This was well above the boiling point of methanol at atmospheric conditions. Because of this a longer residence time would be needed due to the lower availability of methanol.

2.5.1.2 Base

When a base catalyst is used, the base will deprotonate the alcohol. If there is water in the system there will be an undesirable hydrolysis. Therefore, the reaction needs to be kept dry.

The reaction takes place as in Figure 16. 1) The base deprotonates the alcohol. 2) The nucleophile attacks the carbonyl carbon, forcing the electrons to the oxygen. 3) The oxonium ion electrons come back down to the carbonyl carbon kicking off the original RO^- group. 4) The free RO^- group attacks the water molecule that originally deprotonated the alcohol, thus reforming the base catalyst.

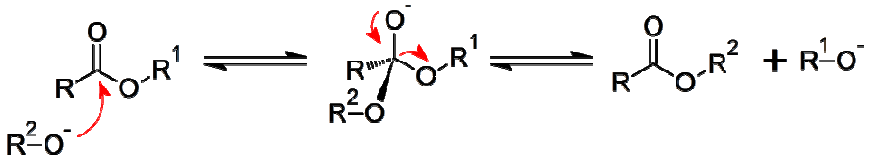

Figure 16 Base catalyst mechanism [11]

However, when making biodiesel this transesterification reaction must take place three times. The first reaction will reduce the triglyceride to a diglyceride and biodiesel molecule. Then the reaction will reduce the diglyceride to a monoglyceride and biodiesel molecule. Finally the reaction will occur a third time reducing the monoglyceride to glycerol and biodiesel

molecule. This results in the consumption of three alcohol molecules and an oil molecule and produces three biodiesel molecules and a glycerol. The catalyst was consumed and then generated again in each of these steps. Figure 17 illustrates this process.

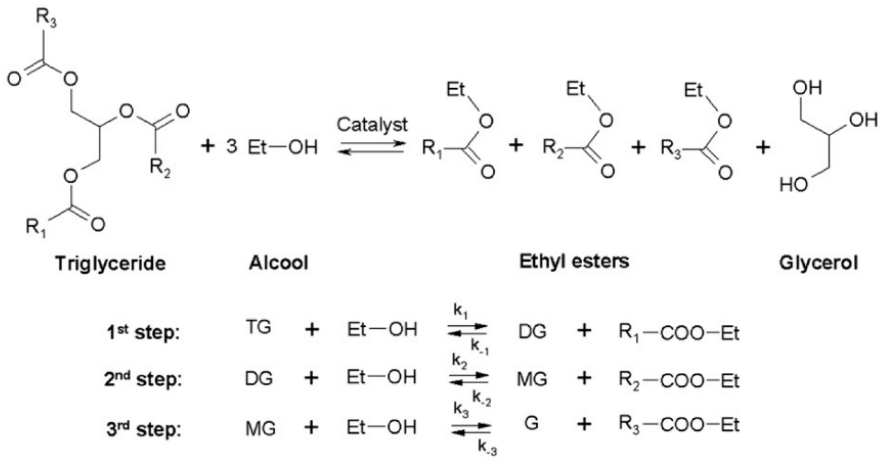

Figure 17 Reaction scheme for biodiesel transesterification[24]

Similarly to the batch reaction the optimal concentration of homogeneous base catalysts is about 1 wt%.[21] The reaction temperature with base catalyst is usually kept low, as when temperature increases in this reaction more saponification occurs. Richard et al. used EtONa as the catalyst with a 6:1 methanol to oil molar ratio and a reaction time of 15.71 minutes in a microtube reactor to obtain an ethyl ester content of 96.0%.[13] Wen et al. was able to achieve a 97.3% yield in Zigzag-1 using 6:1 molar ration of methanol to oil at 60ºC and KOH as the catalyst.[19]

2.5.2 Heterogeneous

Heterogeneous catalysts do not involve mixing any substance in with the alcohol, but rather are fixed to the surface of the walls of the microreactor. This is a less costly and simpler separation process. With the homogeneous base catalyst, soap is formed from the reaction and must be separated out. By using heterogeneous catalysts there is no soap formed; therefore, there are less separation costs. There is still glycerol that is a byproduct of all the transesterification reactions with a triglyceride as a reactant. The heterogeneous catalyst is preferred, because of the resulting simpler and cheaper separation processes.[21]

Usage of heterogeneous catalysts in a microreactor is hardly seen, though CaO has been used for biodiesel production.[21] This however turned out to be problematic. The calcium gets dissolved into the alcohol, and then would need a separation reaction. Leaving the calcium in the product would not be an option as calcium will build up in an engine if burned.

2.5.3 Catalyst-Free

Trentin et al. performed transesterification of soybean oil (SBO) at supercritical ethanol conditions in a continuous catalyst free process using carbon dioxide as a co-solvent.[25, 26] The reaction was conducted by using two microtube reactors with an internal volume of 37.9 mL and 24.9 mL with an internal diameter of 0.775 mm and 0.571 mm, respectively. These microtubes were made of stainless steel with an outer diameter of 1/16”.

The reaction involved placing the ethanol and oil in an Erlenmeyer flask and mixing the liquids together via a mechanical mixing device. The molar ratio of oil to ethanol was 1:20. The liquid mix was fed into the microtube reactor via a HPLC pump at a flow rate of 0.8 mL/min.

Using a syringe pump, carbon dioxide was fed into the system as a co-solvent at a specific rate. The microtube reactor was placed in a furnace where the temperature could be measured and adjusted as needed. A glass vial was used to collect the products. The optimal conditions for the highest yield of ethyl ester were determined to be at a reaction temperature and pressure of 598K and 20 MPa and using a carbon dioxide to liquid mixture mass ratio of 0.20:1. The smaller diameter microtube reactor showed to have a higher FAEE yield compared to the larger diameter reactor.

This experiment has proven to be successful in producing FAEE. However, this process involves a high cost to maintain and large energy usage. This process is less cost effective than other processes to synthesize biodiesel.

2.6 UTC Biodiesel Synthesis

At UTC the microreactor research group uses vegetable oil and methanol as reactants and nickel oxide (NiO) as a solid heterogeneous catalyst. This poses the problem of having a two-phase system. Nonetheless, the system was studied with positive results, using stirred-tank reactors and high temperature stainless steel vials.[6, 7] To try and overcome the phase barrier a co-solvent is used to mix the soybean oil and methanol into one phase. The co-solvent used is oleic acid, a free fatty acid.[27]

Free fatty acid is a long carbon chain with a carboxylic acid group at one end. Oleic acid has 18 carbons, as compared to diesel having 12-20 carbons. The free fatty acid will undergo the esterification reaction to produce a FAME molecule and water. Figure 18 shows the reaction. It was discovered that a 1:1:1 volume ratio of the soybean oil to free fatty acid to methanol yielded the best miscibility.[6, 7] So the 1:1:1 feedstock is studied.

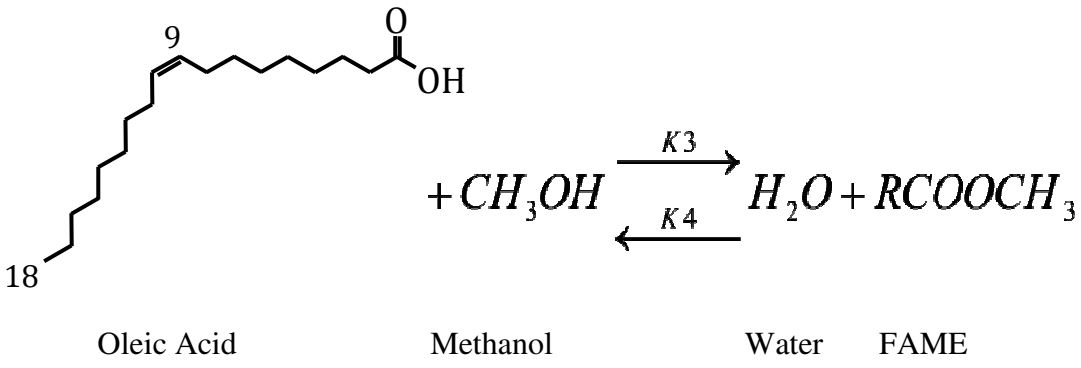

Figure 18 Transesterification Reaction with a Free Fatty Acid[6]

There are several methods used to study the biodiesel production: stirred-tank reactors, stainless steel vials, and microreactors. These processes are detailed in section 3 Methodology.

CHAPTER 3

METHODOLOGY

In this section the methods to collect data will be discussed. The methods include measuring density, viscosity, stirred-tank reactors, stainless steel reactors, purification, microreactors, and analytical chemistry.

3.1 Measuring Density

The one-phase feedstock is a mixture of soybean oil, free fatty acid, and methanol[28] in a 1:1:1 volume ratio. The method of measuring a known amount of volume and weighing that volume was used. This volume was measured using a 2 mL class A glass analytical pipet, then weighed on a scale. The procedure is as follows.

1) Heat a water bath to the desired temperature, room temperature to 64°C, using the EchoTherm Programmable Multi-position Stirring Hot Plate.
2) Place the vial of liquid in the water bath and let the temperature equilibrate. Test the temperature of the liquid in the vial compared to the water bath.
3) Tare the 2 mL class A pipet, and fill pipet with vail liquid to the appropriate mark.
4) Weigh the pipet with liquid
5) Clean and dry the pipet and repeat the process at each desired temperature.

3.2 Measuring Viscosity

The viscosities of two substances—soybean oil (SBO) and the one-phase feedstock—were measured using a falling ball type viscometer[29], shown in Figure 20. This type of viscometer uses the descent time of a sphere, made of glass, stainless steel, or tantalum, to determine the viscosity of the substance the sphere is flowing through. In order to determine the viscosity, the following relationship must be known to relate time and viscosity. [29]

$$\mu = K(\rho_f - \rho)t \tag{2}$$

Where μ is viscosity (centipoise), ρ_f is the density of the sphere (g/mL), ρ is the density of the fluid (g/mL), K is the viscometer constant, and t is the time it takes the sphere to descend from one pair of lines to the other. The viscometer constant will vary with the size of the viscometer. To determine what size of viscometer is needed an estimation of the viscosity range of the substance is needed. For these substances, the appropriate viscometer was determined to be size number 2 which is scaled for substances in the 2 to 200 centipoise range. The number 2 viscometer has a viscometer constant of 3.3.[29] The procedure is outlined below:

1) Place approximately 5 mL of liquid substance in a small beaker or graduated cylinder.
2) Fill the viscometer with the appropriate fluid until there is approximately ¼ inch of space left at the top. This will prevent most of the spillage when the sphere and the top are added.
3) Select the appropriate sphere and place it in the viscometer. The spheres are made out of three different types of materials, each with its own valid range of viscosity, see Table 2.

Table 2 Viscosity Range of Each Material in Gilmont Viscometer Number 2

Material	**Glass**	**Stainless Steel**	**Tantalum**
Viscosity Range, cp	2 to 20	10 to 100	20 to 200

4) Remove the top cap from the lid assembly to allow air to escape from the viscometer. Tighten the lid assembly onto the viscometer, and then tighten the top cap back onto the lid assembly.

5) Ensure proper assembly by turning the tube up-side-down and making sure no liquid escapes and bubbles do not exist inside the viscometer.

6) An EchoTherm Programmable Multi-position Stirring Hot Plate was used for heating the Gilmont viscometer to the appropriate temperature. To attempt to keep the water bath at a constant temperature throughout the cylinder, a magnetic stir bar was used to mix the water constantly. It is possible to keep the majority of the viscometer in the water bath at all times, see Figure 19.

7) Readings are taken by holding the tube vertically and recording the time it takes for the sphere to fall between the red markings, see Figure 20 for details.

Figure 19 Gilmont Viscometer in Water Bath

Figure 20 Gilmont Viscometer

3.3 Stirred-Tank Reactors

Four 25-mL round bottom flasks (RBF) used as stirred-tank reactors; these were purchased from Sigma Aldrich.[30] The temperature of the stirred-tanks was maintained about 65ºC, methanol's boiling point temperature, by using a water bath heated on an EchoTherm Programmable Multi-position Stirring Hot Plate.[31] The RBFs were not placed in the hot water bath until the water has reached the 70°C. Each RBF is fitted onto its own condenser.[32] Cold water runs through the four condensers in series. The water was determined to be cold enough with a high enough flow rate to ensure proper condensation of the methanol vapor. The stirred-tank reactor set up is depicted in Figure 21. The flasks were filled with a liquid mixture, catalyst (nickel oxide), and a 1 cm stir bar. The liquid mixture was a mixture of soybean oil, free fatty acid, and methanol in a volume ratio of 1:1:1. For the longer experiments, it was determined that methanol boils out of the system at a rate of 1.0 mL per hour. So every 15 minutes 0.25 mL of methanol was introduced back into the system in order to maintain the 1:1:1 volume ratio of the materials. A 1.0 cm magnetic stir bar was placed in each of the stirred-tank reactors at 800 RPM to maintain adequate mixing.

Figure 21 Stirred-tank Reactor Setup

3.4 Stainless Steel Vials

Eight stainless steel vials were used as high temperature unstirred reactors. The reactors are 5 mL Retsch Mixing Jars purchased from the Gilson Company.[33] Temperatures as high as 180°C were reached by using a 20GC Gravity Convection Oven from Quincy Lab, Inc.[34] According to a standard cox chart methanol's vapor pressure is approximately 26 atmospheres at 180°C. The vials were specially chosen to withstand this high pressure. The threads of the vials were wrapped two to three times with Teflon plumbing tape to ensure a proper seal. 3 mL of 1:1:1 volume ratio of soybean oil to free fatty acid to methanol were placed in each vial with 0.103 g of nickel oxide, which is 3 wt%. The cap was then tightly screwed into place to ensure a proper seal. The vials were then placed in the oven around the mercury thermometer. When the reaction time has been met the vials were quenched in water to stop the reaction. The stainless steel vials are depicted in Figure 22.

Figure 22 Stainless Steel Vials

3.4.1 Heating Time

For using the stainless steel vials an important part of the analysis is time it takes to heat up to temperature. The following approach was used.

1. Fill the vials with 3 mL of soybean oil.
2. Place the vials in the pre heated oven, either 65 or 180°C, without the caps on them
3. Place the mercury thermometer in the liquid, checking that the thermometer is not touching the metal, only in the liquid.
4. Take readings of the temperature every minute till it equilibrates.

3.5 Purification

Samples produced from the stainless steel vials and the stirred-tank reactors had to be purified, and the solid catalyst separated from the liquid. This was accomplished was by a centrifuge. The maximum amount was transferred into the 10 mL centrifuge vials. The vials are then centrifuged at maximum speed of 6000 rpm, for one hour using a Hermule Z206A centrifuge[35], seen in Figure 23. The middle layer was decanted using a glass Pasteur Pipet into a small vail for analysis. The top layer is methanol, the middle layer is oily products, and the bottom layer is glycerin. During the decanting process special care was taken not to disturb the nickel oxide pellet. The time it takes for separation to occur can be calculated by using Stokes' Law for spheres which is:

$$\mu = \frac{[2 * R^2 * (\rho_s - \rho) * g]}{9 * v_t} \quad (3)$$

In equation 3, μ is the viscosity of the fluid, R is the radius of the falling particle, ρ_s is the density of the particle, ρ is the density of the fluid, g is gravity, and v_t is the terminal velocity. By solving for the terminal velocity, the time can be determined for how long it will take a particle to fall. This equation can only be used if the Reynold's number is less than 1, which implies creeping flow.[36] The nickel oxide catalyst has a particle size less than 50 nm. In this case creeping flow is an adequate assumption.

Figure 23 Hermule Z206A Centrifuge

To purify the samples for analysis, the methanol that is in solution still must be removed. Due to the fact that oil and methanol have a significantly different boiling point, the methanol is boiled out of solution. When the solution temperature rises above 65°C methanol is fully removed. The samples are then cooled and await analysis.

3.6 Microreactors

Microreactors were manufactured by Johns Hopkins University using designs from the UTC microreactor research group.[4] The channels of the microreactors are coated with Nickel (II) Oxide, a base catalyst. The nickel oxide was applied using a technique known as magnetron sputtering. Three microreactors were made; two of them are considered wavy reactors, and the other one is a straight channel. These are seen in Figures 24 and 25. In all the reactors the microchannel size is 50 µm by 500 µm. The length of the wavy reactor channels are 15 cm, and the straight reactor channel length is 3 cm. In each of the straight parts of the reactors there are triangular shaped objects that assist in mixing.[4]

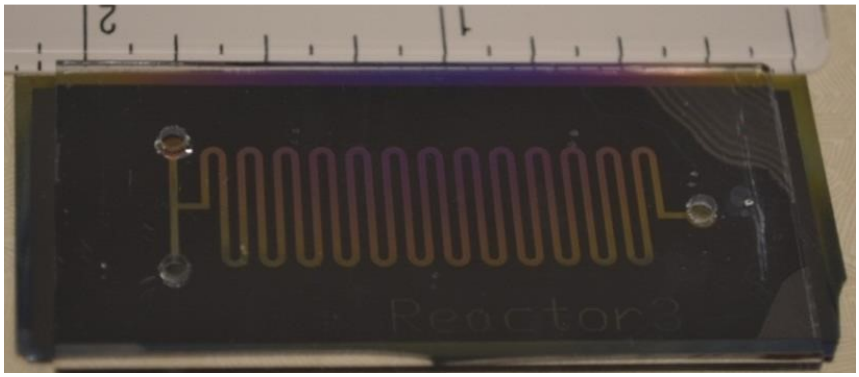

Figure 24 Wavy Microreactor

Figure 25 Straight Microreactor

Due to the channel size being so small low flowrates must be used. The flow rates used where from 1 µL/min up to 40 µL/min. The microreactors were tested up to a flow rate of 450 µL/min without failure. The Cole-Parmer Touch-Screen Syringe Pump is used to achieve exact, steady flow rates. The lowest flow rate achievable for this pump is 5 picoliters/minute. The setup is shown in Figure 26. There was a change to this setup in order to relieve the stresses in the system, see Figure 27. The microreactors were placed vertically and attached to the side of the Plexiglas stand, with the inlets on top and the outlet on the bottom. A resistance heater was attached to the rear of the microreactor to add heat to the system when desired. The reactor was insulated on the back in order to achieve better heat transfer from the heater.

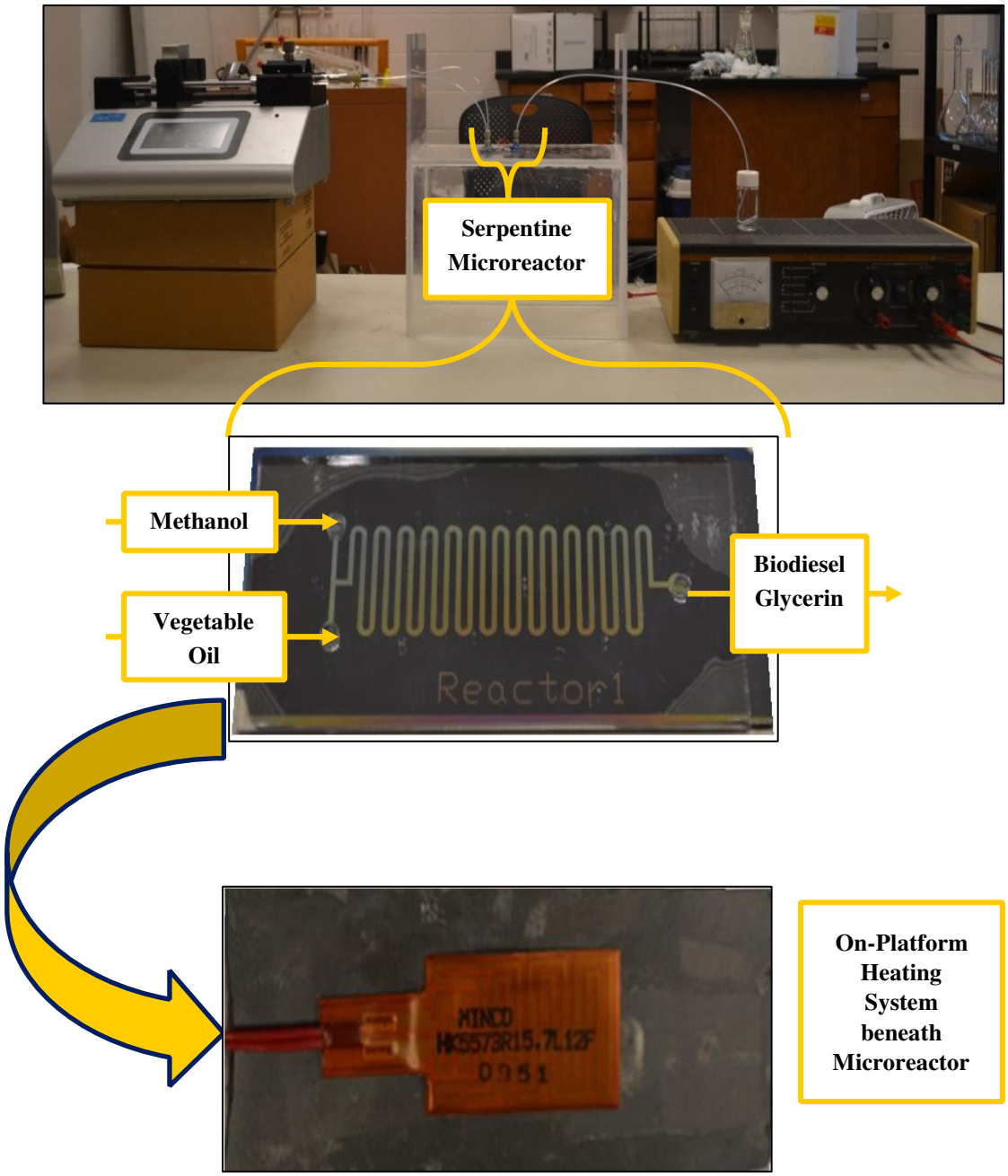

Figure 26 Top picture, is the experimental set up with reactor horizontal. Middle picture is a wavy reactor with the inlets on the left, and the outlet on the right. The bottom picture is the resistance heater that is attached the microreactor

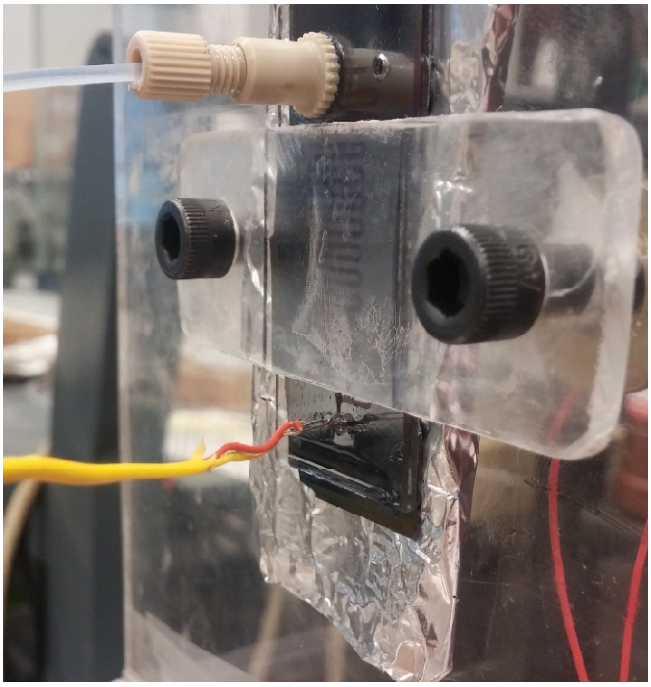

Figure 27 Vertical Apparatus with One Inlet Plumbed and No Outlet Plumbed

3.7 Analytical Chemistry

To analyze the samples from each process, analytical chemistry was performed. The conversion of soybean oil can be found by using gas chromatography coupled with a flame ionization detector (GC/FID). Since soybean oil and free fatty acid appear very similar in GC/FID, another method must be used in order to determine the conversion of free fatty acid. A test called acid number was used to determine the conversion of free fatty acid. The following sections describe each of these processes.

3.7.1 Gas Chromatography

Gas Chromatography coupled with a flame ionization detector was used to analyze the conversion of soybean oil. The chemicals used for this process are n-heptane (≥99.5%)[37],

tricaprin (GC ≥99%)[38], and pyridine (anhydrous, 99.8%)[39], all from by Sigma Aldrich. The column used was a MXT-Biodiesel TG column, 15 m length and 0.32 mm inner diameter.[40] In order to standardize the analysis process, ASTM D6584 was referenced.[41]

When the sample is injected into the gas chromatograph column the substances are separated based on boiling points and how much the sample attaches itself to the coating on the column. In this case the inner coating is siltek. This allows the larger glycerides to stick longer in the column, thus giving the ability to distinguish biodiesel, monoglyceride, diglyceride, and trigylcerides from each other. The sample is forced through the column by helium, a carrier gas which is inert to the samples and the detector. Peak Simple software is used to convert the millivolt reading from the FID into the corresponding concentration. What this does not allow for is distinguishability of biodiesel from free fatty acid. An alternate method will be used to analyze free fatty acid conversion.

Since biodiesel and free fatty acid are so close in structure and cannot be distinguished from each other via GC/FID, the amounts of chemically bound glycerin (CBG) was examined. To determine the soybean oil conversion the CBG of the initial sample was compared to the CBG of the sample after a reaction.[42] The CBG is calculated using Equation 4.

$$CBG = \frac{(Triglycerides + Diglycerides + Monoglycerides)}{Tricaprin} \quad (4)$$

Equation 4 explains that the sums of the each of the glycerides are divided by the area of the tricaprin peak generated from the GC/FID and Peak Simple software. Using this equation to determine the CBG, the conversion of can then be calculated by Equation 5.

$$CBG\ Conversion\ (\%) = \frac{(CBG_i - CBG_t)}{CBG_i} \quad (5)$$

In Equation 4 the CBG_i represents the CBG present initially, while CBG_t represents the amount of CBG present in the sample after time t.[42] The GC/FID is shown in Figure 28. The procedure for using the GC/FID is as follows.

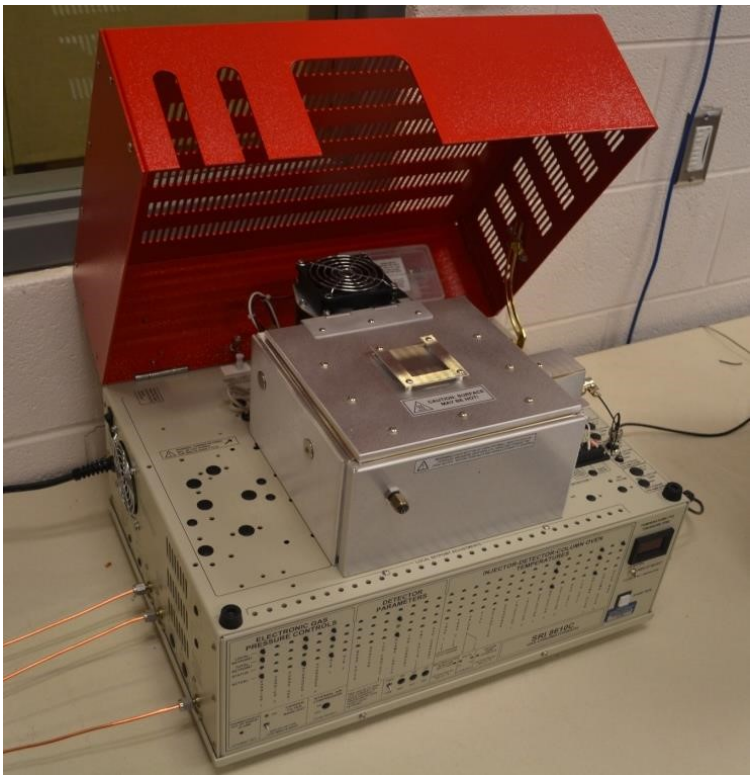

Figure 28 SRI 8610C GC for FAME Analysis from Triglycerides

1. Open the valves to allow for flow of hydrogen, helium, and compressed air gases.
2. Turn on the GC/FID along with Peak Simple software. Allow the FID to reach operational temperature
3. Measure out 0.100 g of sample after the purification process into an 8 mL vial.

4. To the 8 mL vial add 100 µL of tricaprin an internal standard
5. Also add 100 µL of n-methyl-n-(trimethylsilyl) trifluoroacetamide, MSTFA.[43] This step is critical because certain functional groups are known to cause problems with this column inner coating. The groups consist of carboxylic acids, amines, thiols, and hydroxyl groups. MSTFA will undergo a reaction replacing these functional groups with an alkylsiyl group such as $SiMe_3$. This makes compounds with these functional groups more stable and less volatile, helping improve GC analysis.[44]
6. Let the mixture react for 20 minutes
7. Add 8.0 mL of n-heptane to the vial and mix.
8. Measure 1.0 µL of the sample and inject into the GC.
9. Start the Peak Simple software analysis.
10. When Peak Simple analysis is complete export the area data into Excel using the CBG equations determine the CBG conversion.

3.7.2 Acid Number Analysis

Since free fatty acid cannot be distinguished from FAME on the GC/FID an alternate method must be used to determine how much free fatty acid persists in the samples. This is done using a method of acid number analysis, defined by ASTM D974.[45] This method was slightly adjusted to be more accurate for the small quantities. The 0.1 N potassium hydroxide was diluted to 0.01 N.[46] The acid number is determined by neutralizing the free fatty acid in the sample, a titration with potassium hydroxide. All the chemical used were supplied by Sigma Aldrich: 0.1 N potassium hydroxide in isopropanol, 2-propanol (anhydrous, 99.5%)[47], toluene (anhydrous, 99.8%)[48], and α-naphtholbenzein.[49] Acid number and free fatty acid conversion are defined in Equations 6 and 7.

$$Acid\ Number = \frac{mg\ KOH}{g\ Analyte} \tag{6}$$

$$FFA\ Conversion = \frac{AN_i - AN_t}{AN_i} \tag{7}$$

In order to titrate, an indicator must be used to determine when the all of the free fatty acid has been used up. This process used 0.01 N potassium hydroxide, KOH, to neutralize the free fatty acid. The indicator used was α-naphtholbenzein, which in the presence of free fatty acid appears as an orange color, Figure 29, and in the presence of a base appears as a green, Figure 30. A titration solvent must be prepared before analysis. This solvent consists of toluene, isopropyl alcohol, and water in a ratio of 100: 99: 1. The analysis follows these outlined steps:

1. Measure 0.1 to 0.5 g of the sample after purification into a 250-mL Erlenmeyer flask.
2. Add to the flask 10.0 mL of titration solvent.
3. Add to the flask 0.50 mL of the indicator, a solution of 10g α-naphtholbenzein per 1 liter of titration solvent. At this point the sample should be orange, Figure 29.
4. Add to the flask the 0.01 N KOH slowly until a green color persists. Record the amount of KOH used.
5. Determine the mass of KOH added to the solution using Equation 8. where MW_{KOH} is the molecular weight of KOH

$$Mass\ KOH, mg = mL\ of\ KOH\ added * 0.01\ N * MW_{KOH} \quad (8)$$

6. Determine the acid number using Equation 6. And the free fatty acid conversion using Equation 7.

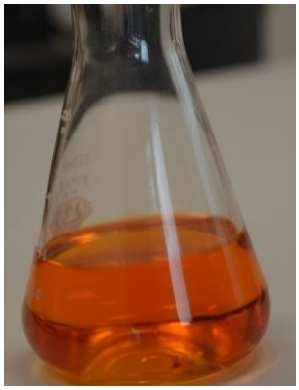

Figure 29 Indicator Orange Color in the Presence of Free Fatty Acid

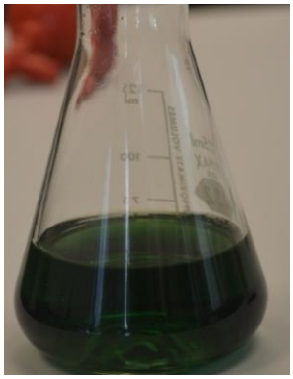

Figure 30 Indicator Green Color in the Presence of a Base

CHAPTER 4

RESULTS

4.1 Density

The densities of the 1:1:1 (soybean oil: free fatty acid: methanol) mixture and pure soybean oil were determined by following the procedure outlined in section 3.1. The soybean oil was measured at 20°C, with four samples being taken and the average of them being reported in Table 3.

Table 3 Density of Soybean Oil at 20°C

	Temperature	Density
Soy Bean Oil	20°C	0.881 ± 0.02g/mL

For the 1:1:1 (SBO:FFA:MeOH) feedstock the temperature varied between 25°C and 64°C. In most cases only one measurement was taken. The data is found in Figure 31. It can be seen that as the temperature increases the density decreases. This is expected as temperature is inversely related to the density.

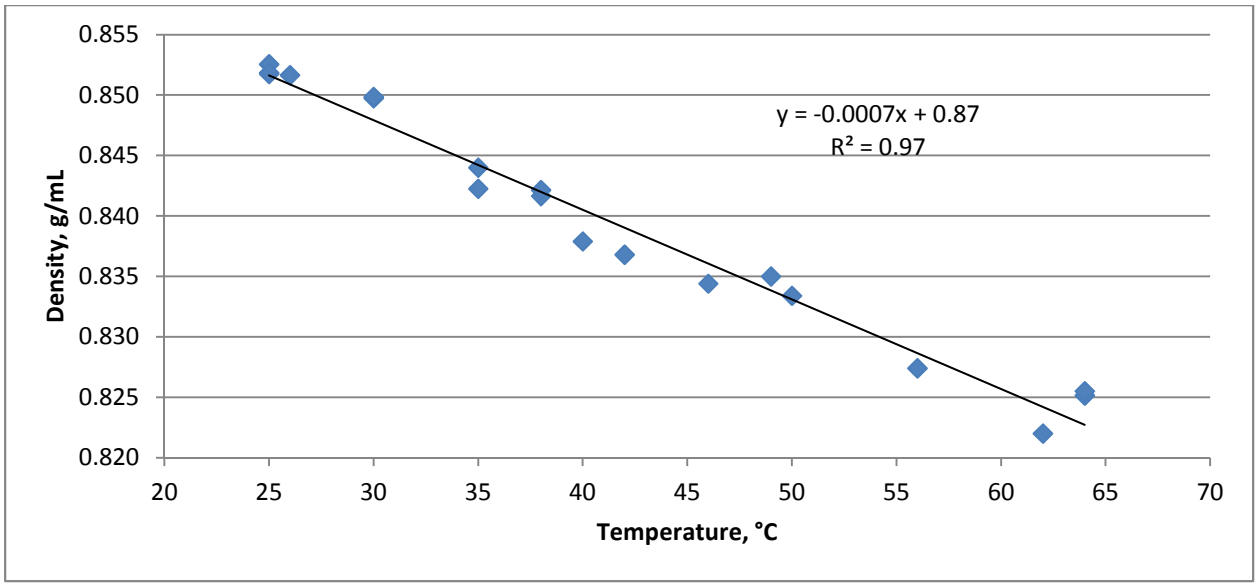

Figure 31 Density vs Temperature of 1:1:1 (SBO:FFA:MeOH) Solution

A linear relation was determined from this data.. This relation is Equation 9. This equation will be used to determine the viscosity of the 1:1:1 (SBO:FFA:MeOH) solution.

$$Density = -0.0007(Temperature) + 0.87 \quad (9)$$

4.2 Viscosity

Following the procedure outlined in the 3.2 the viscosities of the soybean oil and the 1:1:1 (SBO:FFA:MeOH) solution were measured. For the soybean oil the viscosity was found at room temperature only, 20°C. This was accomplished by using a steel ball and a number 2 Gilmont viscometer. The density of the soybean oil is found in Table 3. There were at total of 10 measurements taken and the reported value is the average of them.

Table 4 Soybean Oil Viscosity at 20°C

	Temperature	Viscosity
Soy Bean Oil	20°C	55.05 ± 0.8 cp

When measuring the viscosity of the 1:1:1 (SBO:FFA:MeOH) solution a number 2 Gilmont tube was used in conjunction with a glass ball, due to the low density of the solution. The results of the viscosity measurements are shown in Figure 32.

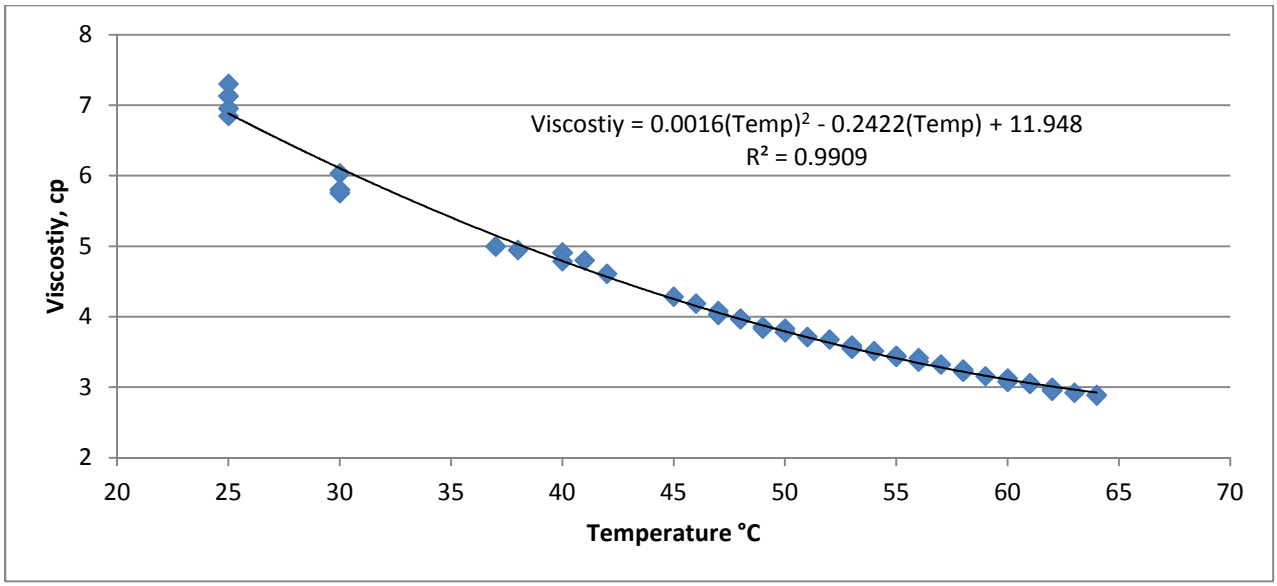

Figure 32 Viscosity vs Temperature of the 1:1:1 (SBO:FFA:MeOH) Solution

A relationship can be determined from this data. The relationship is found as Equation 10. This equation will be used in determining Reynold's number values.

$$Viscosity = 0.0016(\text{Temperature})^2 - 0.2422(\text{Temperature}) + 11.948 \quad (10)$$

4.3 Reynold's Number of Microreactors in This Study

Reynold's number is a dimensionless group that characterizes fluid flow. The range of interest is the lowest values of Reynold's number, below 1. This range is considered to be creeping flow. To calculate Reynold's number Equation 11 was used.

$$Re = \frac{\rho v d}{\mu} \quad (11)$$

In Equation 11, ρ is the density of the fluid, μ is the viscosity of the fluid, d is the diameter, and v is the velocity of the fluid. Since the microreactor is not a cylinder the diameter chosen is for a wide duct system,[50] specifically twice the distance from the bottom to the top plates—100 μm. The flow rates vary from 1 uL/min to 50 uL/min which are the microreactor's practical flow limits. To use Equation 11 for Reynold's number the flow rates need be converted into velocities. This is done by dividing the flow rates by the area of the inlet to the microreactor, 50 um by 500 um or 25,000 um^2. Reynold's numbers are calculated for each temperature and flow rate shown in Figure 33.

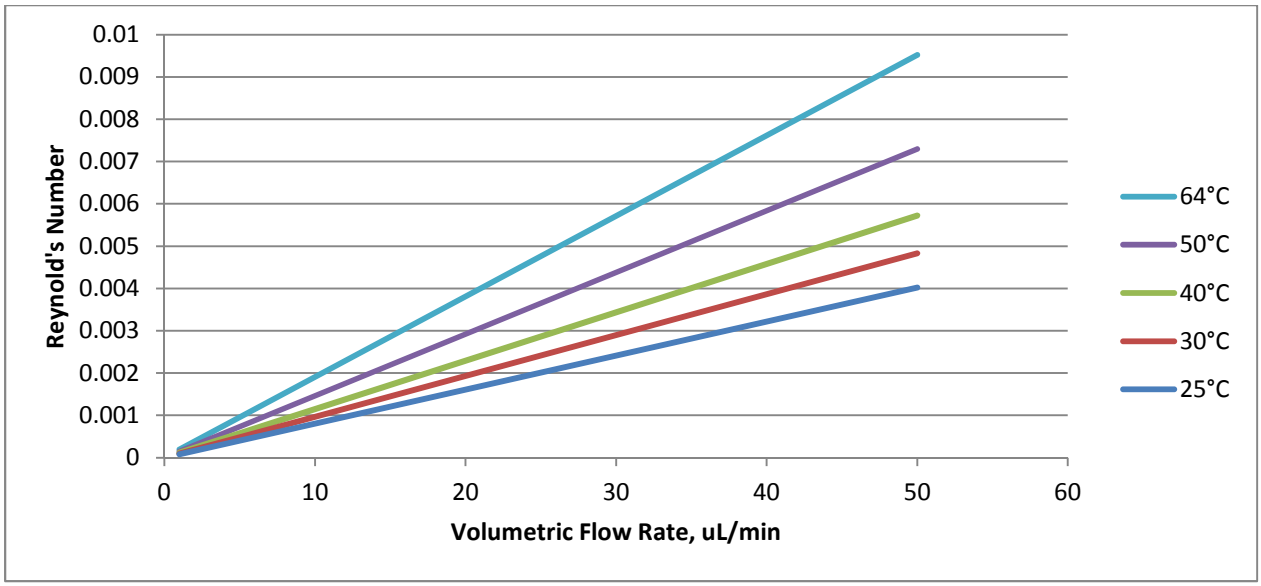

Figure 33 Reynold's number vs Volumetric Flow Rate with Temperature comparison

At the boiling point of methanol, 64.5°C, the Reynold's number does not reach 0.01. A Reynold's number less than 0.1 is indicative that creeping flow persists. This confirms the main mode of mixing is diffusion in the microreactor system.

4.4 Stirred-Tank Reactors

The experiments that used the stirred-tank reactors followed the methods that were described the 3.3. Specifically the water bath was kept at or above 65℃ to ensure methanol was at its boiling point or above. This was visually checked by seeing bubbles in the round bottom flask. Limited data were gathered. The data are displayed in Figures 34 and 35.

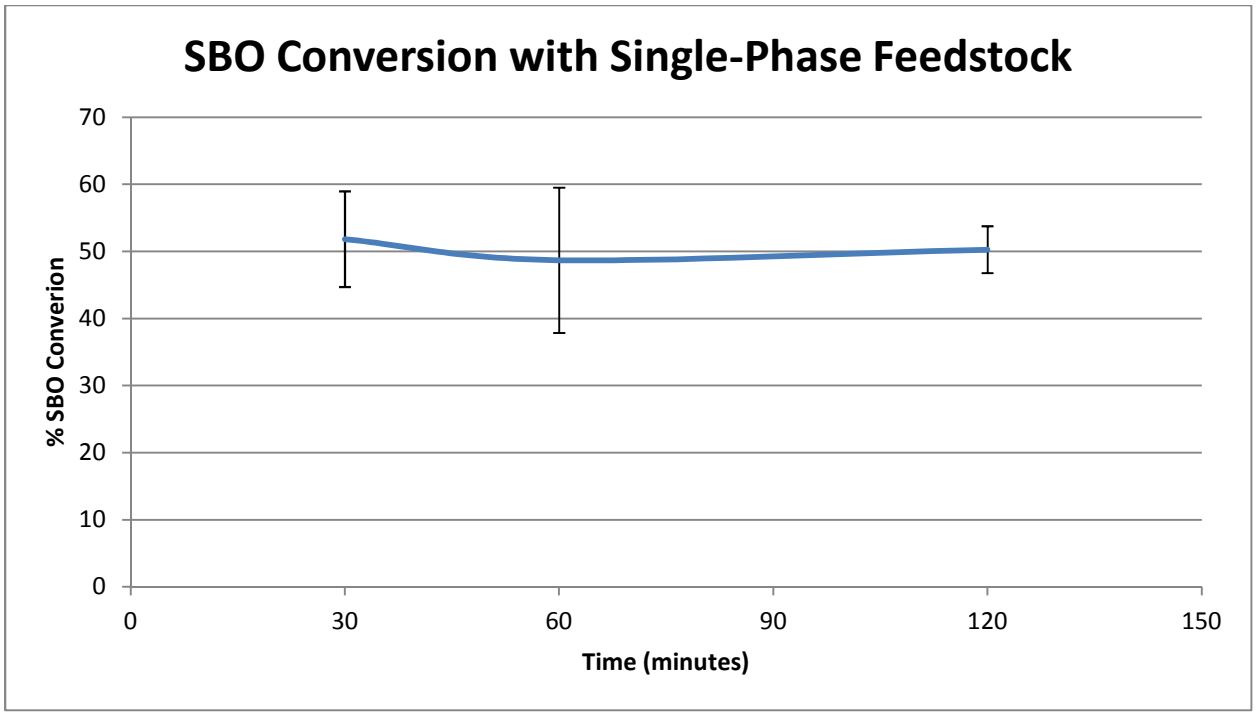

Figure 34 Stirred-tank Reactor, 1:1:1 (SBO: FFA: MeOH), SBO Conversion

Figure 34 shows the 1:1:1 (SBO: FFA: MeOH) solution being reacted in the stirred-tank reactors from 30 minutes to 2 hours. This seems to reach an equilibrium point before the 30 minute mark at about 50% conversion of soy bean oil. There was no 4 hour data collected because of the equilibrium conversion reached.

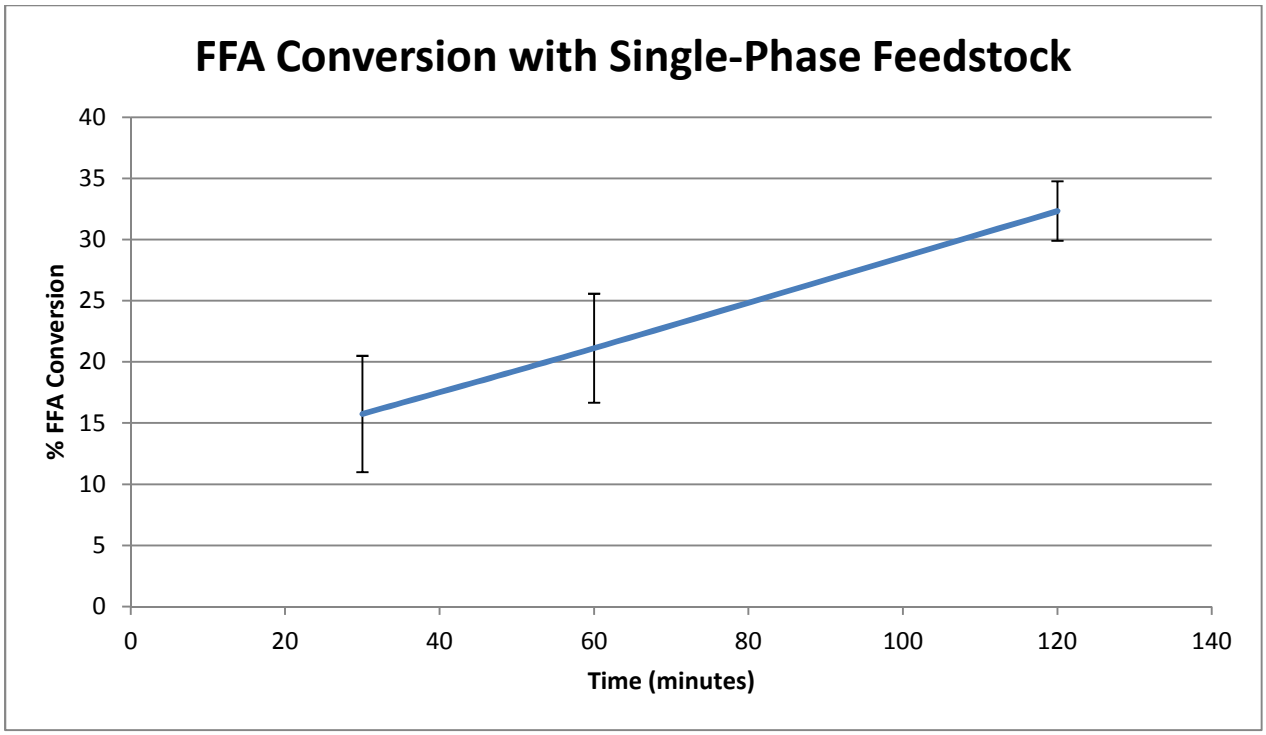

Figure 35 Stirred-tank Reactor, 1:1:1 (SBO: FFA: MeOH), FFA Conversion

Figure 35 shows the 1:1:1 (SBO: FFA: MeOH) solution being reacted in the stirred-tank reactors from 30 minutes to 2 hours. There is a steady increase in the conversion of free fatty acid. It may continue to increase after two hours, but no measurements were taken after two hours

4.5 Stainless Steel Vials

The procedure outlined in section 3.4 was followed in order to obtain the conversions in stainless steel vials.

4.5.1 Heating Time

The heating tests are a rough estimate of the actual temperatures obtained inside the stainless steel vials over time. They may not be completely accurate because the conditions were changed. Some notable differences is that the caps are left off in order to get the temperature of the liquid, and the liquid is completely made up of soybean oil and not the 1:1:1 (SBO: FFA: MeOH) solution. The liquid choice is because when the temperature rises above 65°C the methanol in solution will evaporate thus lowering the systems mass. In order to keep the volume the same, only soybean oil was chosen. So without the cap may increase the rate the temperature is increased due to convection directly with the liquid; but using only soybean oil will decrease the rate the temperature increases due to more mass. With these ideas in mind, the results are shown Figure 36. With the cap on the pressure will increase, this is another condition that was changed.

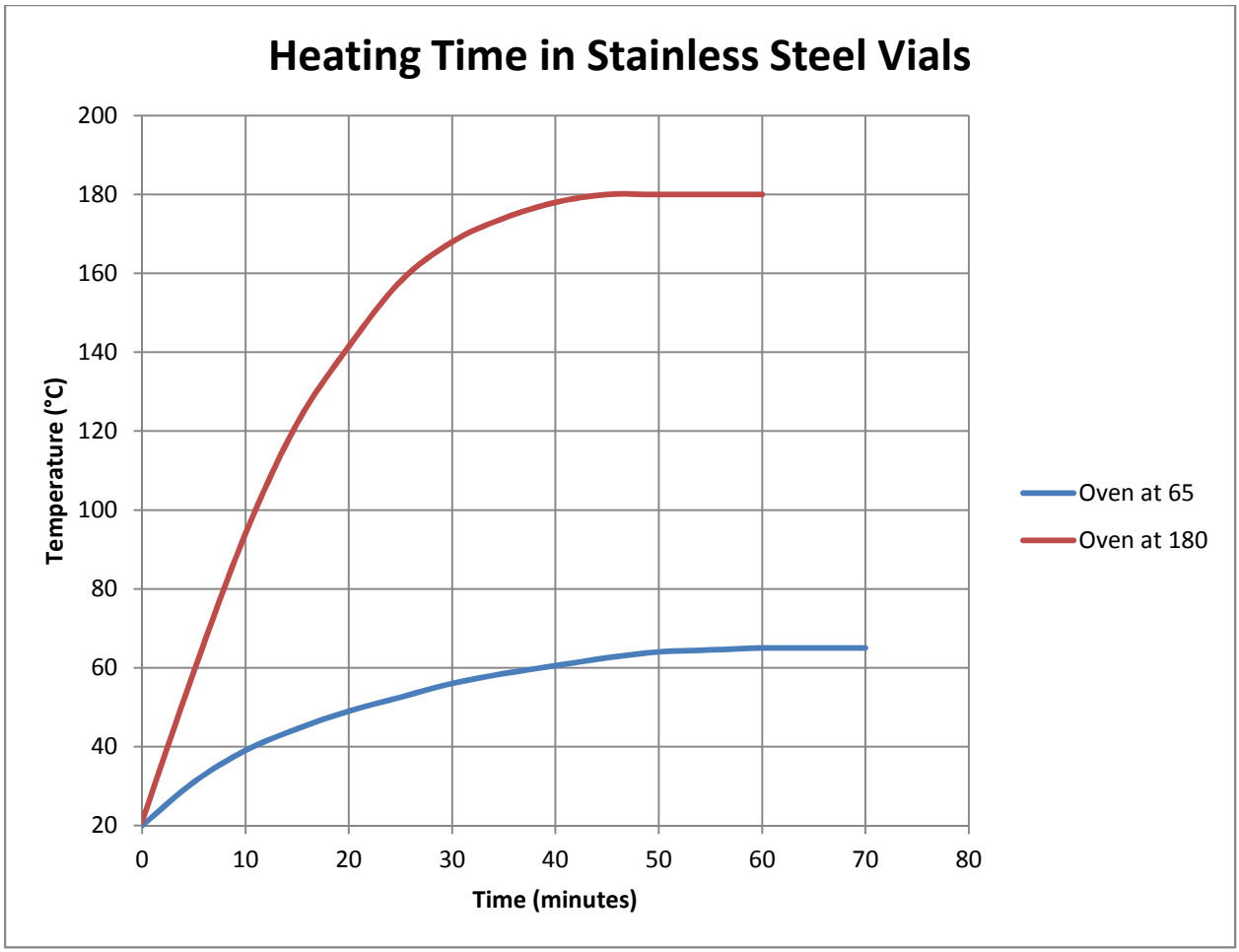

Figure 36 Heating Data with Stainless Steel Vials

Figure 36 shows that when the oven is set at 180°C it will take the liquid inside the stainless steel vials approximately 47 minutes to heat up to an equilibrium temperature. When the oven is set at 65°C the liquid inside the stainless steel vial will take approximately 57 minutes to heat up to the equilibrium temperature. This is of interest because later on the reaction data is collected as low as 30 minutes into the reaction. This means they have not reached the maximum temperature yet by the time the reaction is completed.

4.5.2 180°C Reactions

The stainless steel vials containing the 1:1:1 (SBO: FFA: MeOH) solution were placed in the preheated oven at 180°C and allowed to react for a range of times from 15 minutes up to 4 hours. The 15 minute SBO conversions were deemed as unacceptable due to the low temperature, about 115°C according to the heating test, and the inconsistency of the data collected—error above 60%. Conversions are shown in Figures 37 and 38.

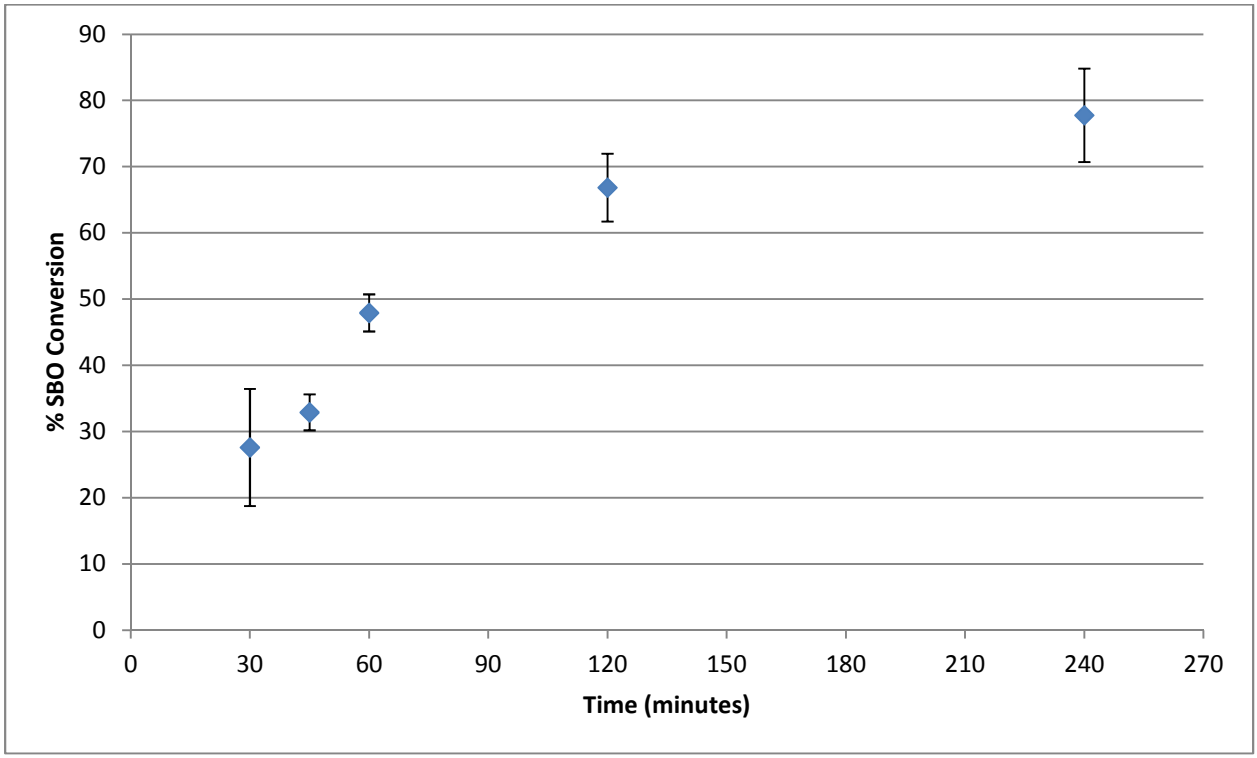

Figure 37 Stainless Steel Vial, 1:1:1 (SBO: FFA: MeOH), 180°C, SBO Conversion

Figure 37 shows the percent soybean oil conversion for the stainless steel vials with the oven temperature at 180°C. The data shows that the SBO conversion seems to level off near the 4 hour mark with a conversion of nearly 80%.

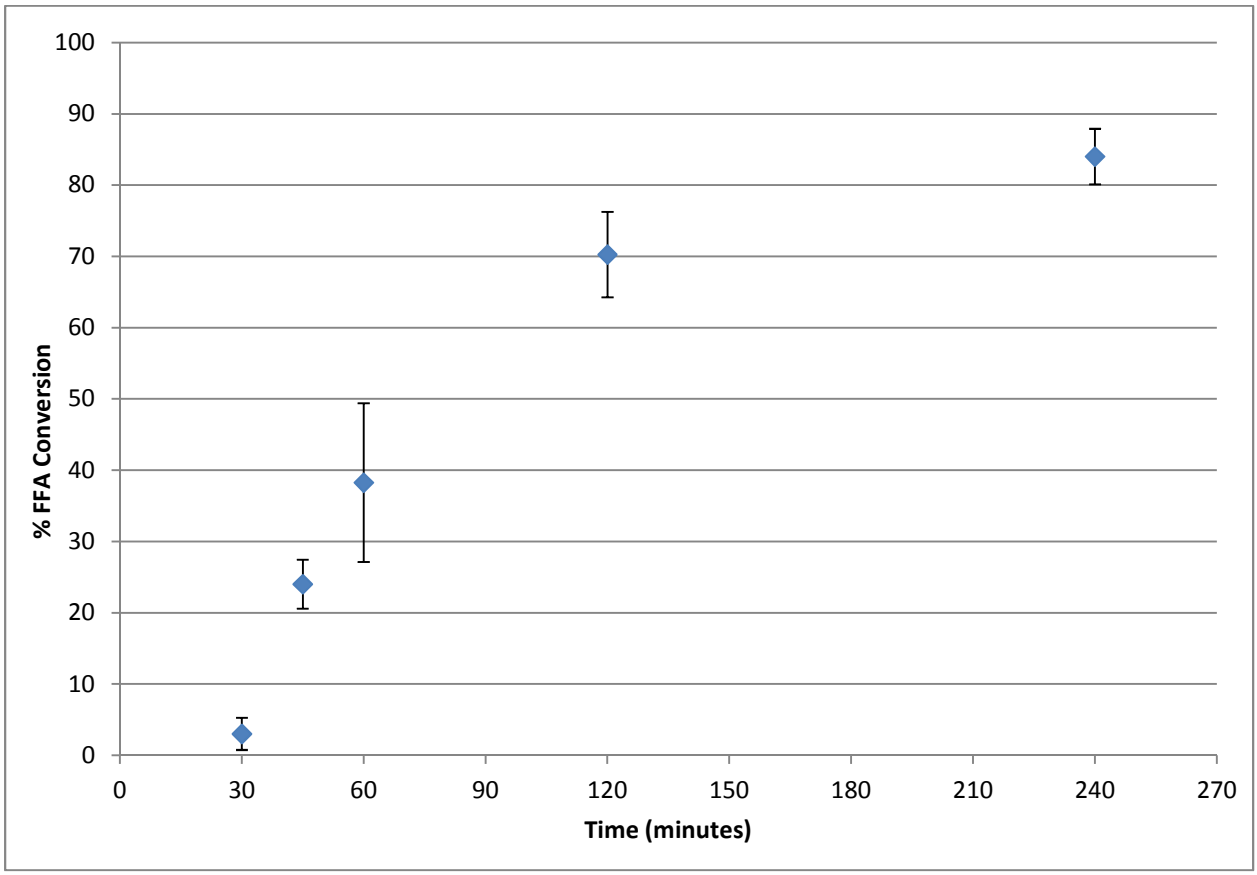

Figure 38 Stainless Steel Vial, 1:1:1 (SBO: FFA: MeOH), 180°C, FFA Conversion

Figure 38 shows the percent conversion of free fatty acid in the stainless steel vials at 180°C. It is shown that the conversion seem to level off around the 85%. This may be slightly higher than the conversion percentage of the soybean oil. Where free fatty acid and soybean oil differ is in the initial reaction rate. Free fatty acid must heat up to a higher temperature for the

reaction to be initialized compared to the soybean oil. At 30 minutes after being placed in the oven soybean oil has an approximate conversion of 28%, while the free fatty acid has an approximate conversion of 4%. But once the solution has reached a higher temperature the free fatty acid reacts readily. FFA may also be more sensitive to the relative low level of methanol present in the single-phase feedstock.

4.5.3 65°C Reactions

The stainless steel vials using the 1:1:1 (SBO: FFA: MeOH) solution were placed in the preheated oven at 65°C and allowed to react for a range of times from 30 minutes up to 4 hours. No data were gathered under 30 minutes due to the reaction temperature being lower than desired. The data are depicted in Figure 39 and 40.

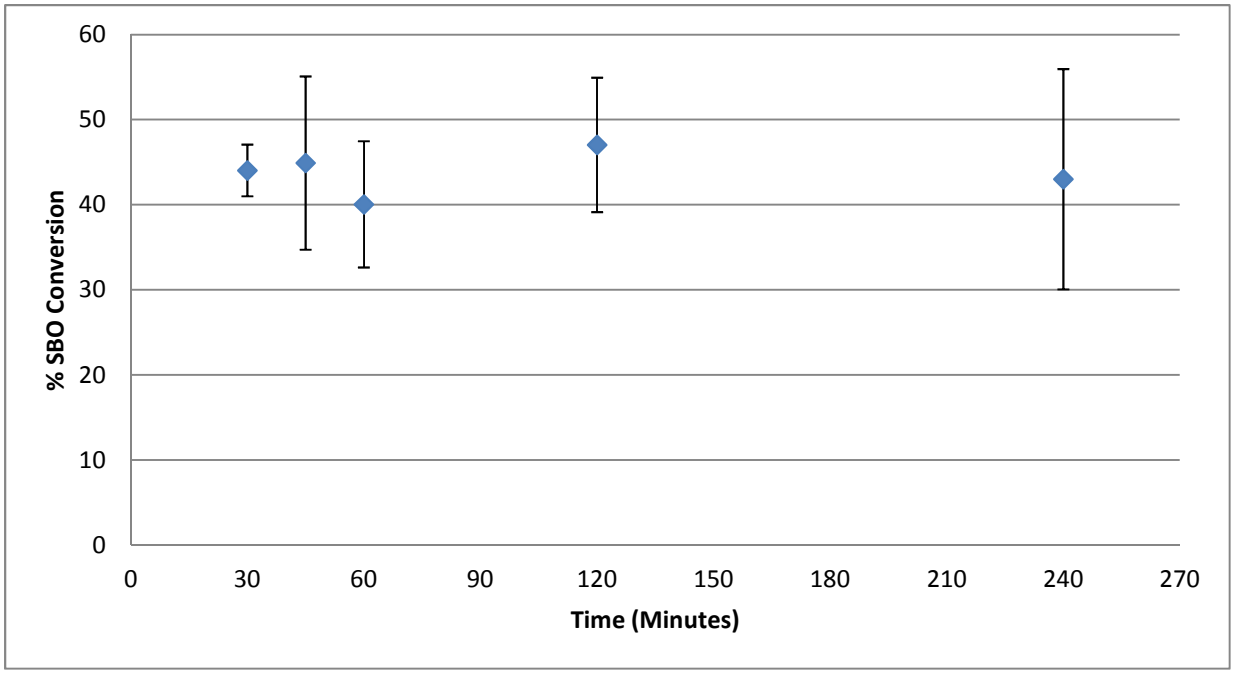

Figure 39 Stainless Steel Vial, 1:1:1 (SBO: FFA: MeOH), 65°C, SBO Conversion

Figure 39 shows the soybean oil conversion of the 1:1:1 (SBO: FFA: MeOH) solution that was placed in a stainless steel vial in a 65°C preheated oven. The conversion seems to reach its maximum very quickly, in less than 30 minutes, at a value of about 45% soybean oil conversion.

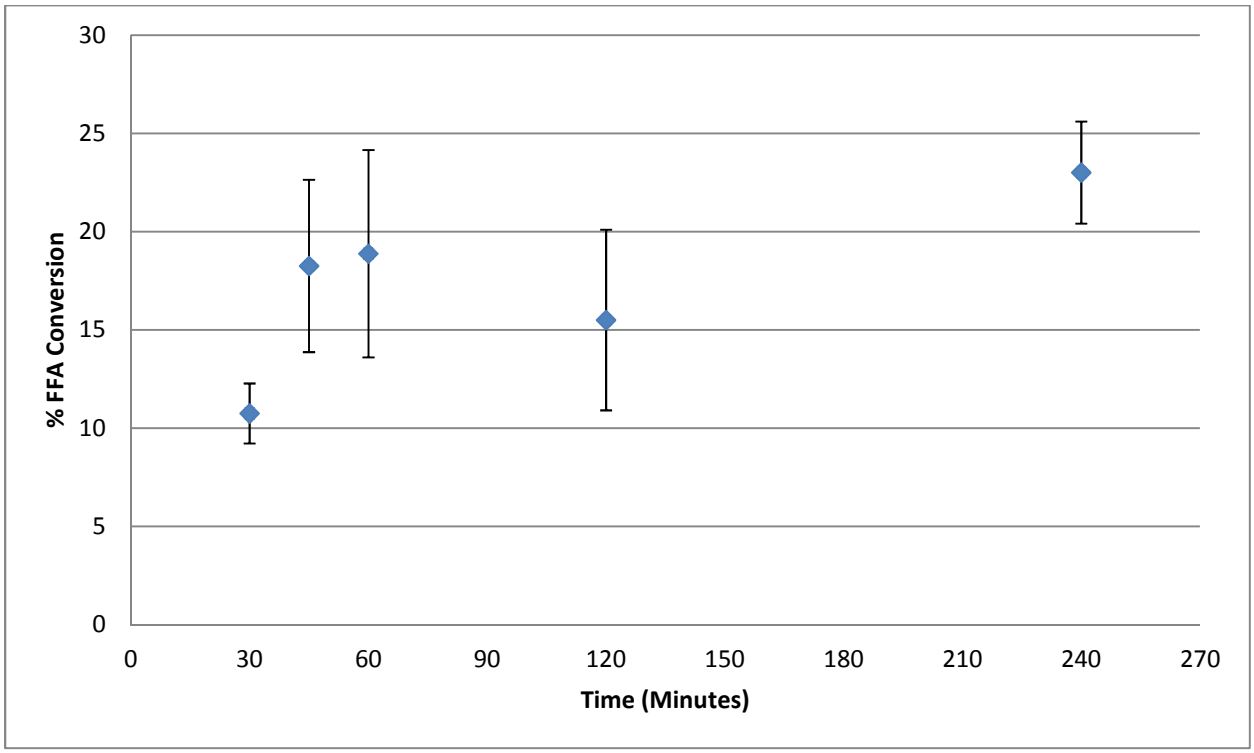

Figure 40 Stainless Steel Vial, 1:1:1 (MeOH: SBO: FFA), 65°C, FFA conversion

Figure 40 shows the conversion percentage of free fatty acid from the 1:1:1 (SBO: FFA: MeOH) solution that was placed in a stainless steel vial in a 65°C preheated oven. The data seem to show a maximum free fatty acid conversion of about 23%.

4.6 Microreactors

Three microreactors were used to collect data. There are two wavy reactors and one straight reactor. The straight reactor was clogged and could not be cleared for analysis. So Reactor 1 and Reactor 2 are both wavy. Reactor 1 was cleared for a short time but then became clogged after two experiments and was not able to be cleared. Reactor 2 was cleared and did not develop a blockage. Reactor 1 results are in Table 5.

Table 4 Reactor 1 Results with 1:1:1 (SBO: FFA: MeOH), Under Boiling Point

Flow Rate	Average Soy Bean Oil Conversion	Average FFA conversion
4 μL/min	5.9%	1%
10 μL/min	0%	3%

Table 5 shows very small percent conversions of both soybean oil and free fatty acid in Reactor 1. This data was taken at a temperature near 65°C, but it did not exceed the boiling temperature methanol, as there were no bubbles observed in the channel. There is very limited data for this reactor due to the channel becoming blocked and was not able to become cleared.

Table 5 Reactor 2 with 1:1:1 (SBO: FFA: MeOH), Under Boiling Point

Flow Rate	Average Soy Bean Oil Conversion	Average FFA conversion
2 μL/min	10.7%	2%
10 μL/min	29.0%	4%

Table 6 shows the percent conversions for Reactor 2. This data was taken at a temperature near 65°C, but it did not exceed the boiling temperature methanol, as there were no bubbles observed in the channel.

Table 6 Reactor 2 with 1:1:1 (SBO: FFA: MeOH), Above Boiling Point

Flow Rate	Average Soy Bean Oil Conversion	Average FFA conversion
2 μL/min	N/A	3%
10 μL/min	24.0%	4%

Table 7 shows the percent conversions for Reactor 2. Data were taken at a temperature near 65°C; the solution exceeded the boiling point of methanol, as there were small bubbles observed in the channel. The bubbles appeared as about 1 mm in length, taking up the entire width of the channel, with had a frequency of 2 bubbles appearing every 2 seconds. A bubble would expand as it traveled through the channel as more methanol vaporized; bubbles had length near 2 mm near the end of the channel.

When comparing Table 6 and 7 (no bubbles vs bubbles), there is no statistical difference in the conversion of free fatty acid. There is a difference in the soy bean oil conversion. This is most likely due the fact there is less methanol available to react in solution; as the bubbles seen are methanol that has vaporized.

Table 7 Reactor 2 with 1:1 (FFA: MeOH), Below Boiling Point

Flow Rate	Average FFA conversion	Residence Time
1 μL/min	14%	3.75 minutes
2 μL/min	19%	1.9 minutes
4 μL/min	14%	74 seconds
10 μL/min	8%	56 seconds

Table 8 shows the percent conversion of free fatty acid with using a 1:1 by volume mixture of free fatty acid and methanol. It also shows the residence time of the fluid with the corresponding flow rate. Data were taken at a temperature near 65°C, but they did not exceed the boiling temperature methanol, as there were no bubbles observed in the channel.

CHAPTER 5

DISCUSSION

5.1 Stirred-tank Reactors

When studying the stirred-tank reactors, two items were examined. First is the effect the co-solvent—free fatty acid—has on the equilibrium conversion of soybean oil. Second is the effect this has on the initial conversion rates. These items are compared between the one-phase (1:1:1, SBO: FFA: MeOH) and two-phase (1:1, SBO: MeOH) feedstocks.

5.1.1 Effect of Co-Solvent with Respect to Equilibrium Conversion

The UTC microreactor research group previously conducted research using the stirred-tank reactors.[6] This was done under the same conditions but used a two-phase feedstock made up of soybean oil and methanol only. The data is shown in Figure 41.

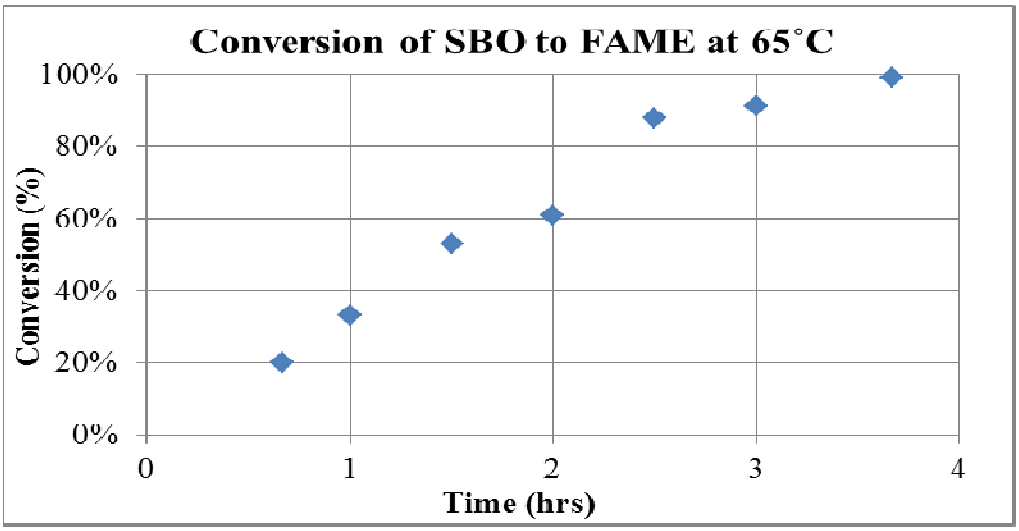

Figure 41 Conversion of SBO in Stirred-tank Reactors, 2 Phase Feedstock[6]

Figure 41 shows that in fewer than four hours in the stirred-tank reactor the conversion reaches 99%. Data were gathered by using an NMR to detect the loss of triglycerides. Using this technique has a tendency to overestimate the yield, due to the fact that the loss of a triglyceride does not mean a molecule of FAME is produced. The triglyceride will convert to di- and mono-glycerides intermediates. The time to reach the maximum conversion is between three and four hours. This is comparable to the industry process using homogenous catalysis.

Now comparing Figure 41 (two-phase) to Figure 34 (one-phase) it can be seen that the conversions of the triglycerides is slightly different. At two hours for the two-phase feedstock the conversion is just about 60%, while with the one-phase feedstock the soybean oil conversion is approximately 50%. However, the main difference between these two sets of data is the relationship with time. For the two-phase feedstock as time increases the conversion increases. But with the one-phase feedstock it seems to have reached equilibrium quickly and stays there with time. This could be due to the availability of the methanol. The two phase feedstock has

more methanol per oil molecule in the system than the one-phase feedstock. Lower conversions may be due to the competition for the methanol. The methanol in the two-phase feedstock only reacts with the soybean oil—glyceride family, while in the one-phase system the methanol must react with the soybean oil and the free fatty acid. So, not only is there not as much methanol in feedstock in the one-phase feedstock but it must also react with more substances.

The results agree with the Le Chatelier's Principle.[51] This principle states, for an equilibrium process, as the concentration of reactants is increased the equilibrium will shift towards the product. In this case when there is a higher concentration of methanol in the system there will be more biodiesel produced.

5.1.2 Effect of Co-Solvent with Respect to Initial Conversion Rates

The UTC microreactor research group previously conducted research using stirred-tank reactors.[7] The data to analyze the initial rates of conversion is shown in Figure 42.

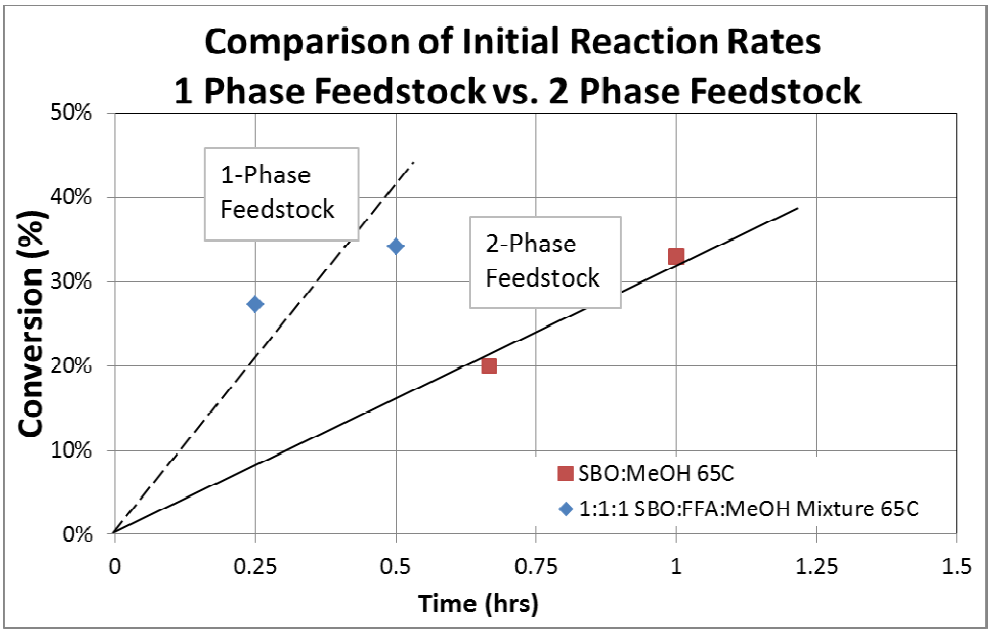

Figure 42 Comparison of Initial Reaction Rates, One-Phase Feedstock vs. 2-Phase Feedstock in the Stirred Tank Reactors[7]

Figure 42 compares the initial rates of conversion of the one and two-phase feedstocks. It shows that the one-phase feedstock has a higher initial conversion compared to the two-phase feedstock. The initial rates for the single-phase feedstock is about double that of the two-phase feedstock after half an hour. This is in spite of the fact that the single phase feedstock has less methanol, the low level of methanol in the feedstock causes the conversions to reach equilibrium quickly and at a relatively low level.

The higher initial conversion can be attributed to the phase boundary being reduced in the one-phase feedstock. In the two-phase feedstock the reaction must take place at the interface of the phases when the catalyst is present, leaving a small volume for the reaction to take place. Whereas, with the one-phase feedstock there is no phase boundary thus allowing for much more volume for the reaction to take place.

This data also confirms Park's ideas of use for a co-solvent.[52] His idea is to use FAME as a co-solvent in the feedstock. This helps with the miscibility of the two phases, made of soybean oil and methanol. Park et al. used KOH as the homogeneous catalyst and FAME as a co-solvent; the UTC research group uses nickel oxide as a catalyst which is heterogeneous and fatty acid as the co-solvent. Data from Park is shown in Figure 43.

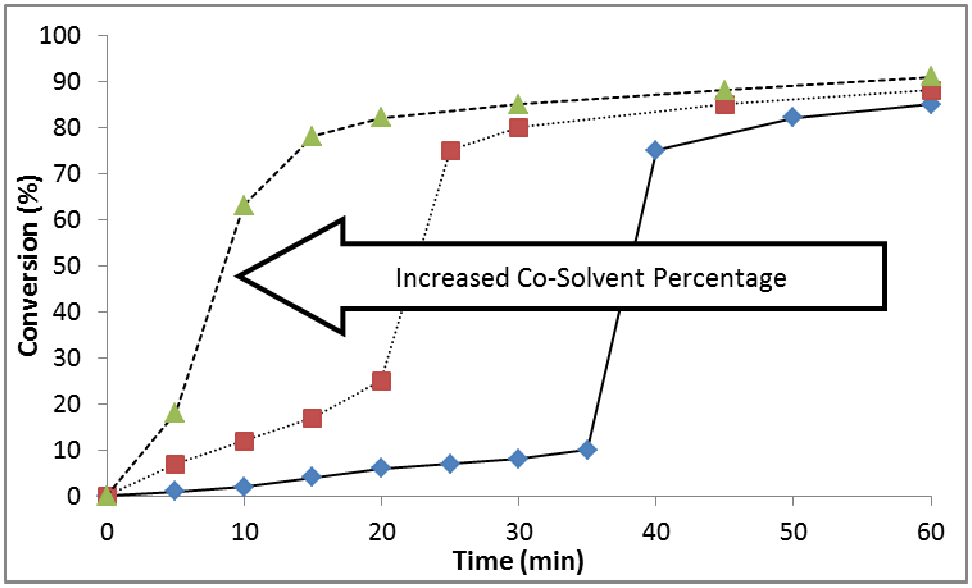

Figure 43 Effect of FAME Co-solvent on the Initial Rates of Conversion to FAME[52]

Figure 43 shows an increase in initial reaction rates with an increase of co-solvent, thus increasing the miscibility. This idea holds true with the heterogeneous catalyst as shown by Figure 42. It is possible to have too much co-solvent which would not maximize the miscibility of the phases,[7] i.e. multiple phases will form.

5.2 Stainless Steel Vials

The stainless steel vial experiments are performed at either 180 or 65°C. From a Cox Chart at the 180°C temperature methanol's vapor pressure will be approximately 26 atmospheres. The reaction process inside of these vials is unclear. There are several challenges that must be overcome. For the reaction to take place, a molecule of methanol and soybean oil (or free fatty acid) must meet at the nickel oxide to react. There is no stirring inside the vials so the nickel oxide settles on the bottom of the vial, with the oil layer above the nickel oxide, then the methanol vapor above the oil. The three phase geometry of make the reaction very difficult for the reaction to take place.

5.2.1 Effect of Co-Solvent with Respect to Equilibrium Conversion

The UTC microreactor research group previously conducted research using the stainless steel vials.[7] This was done under the same conditions but used a two-phase feedstock made up of soybean oil and methanol only. The data are shown Figure 44.

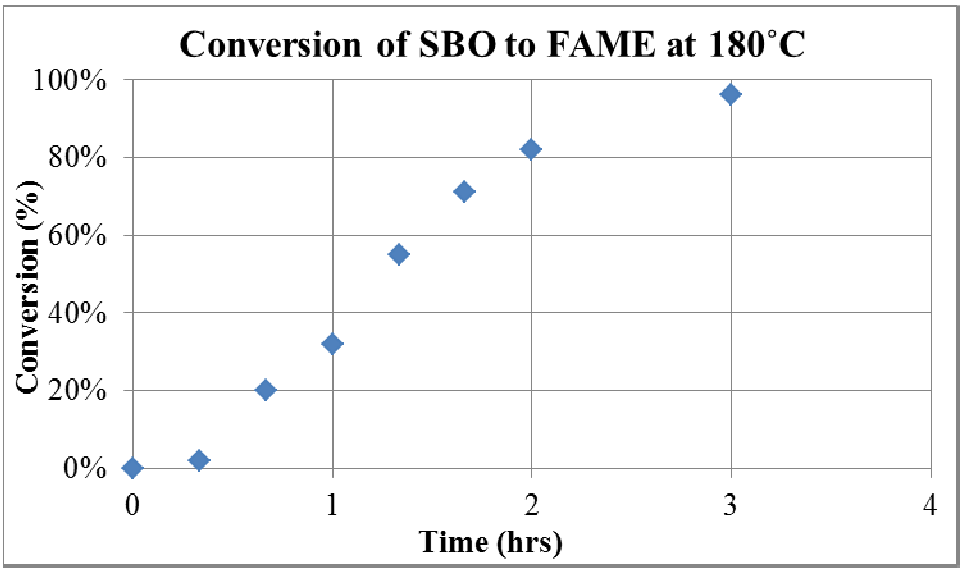

Figure 44 Conversion of SBO to FAME at 180°C[7]

From Figure 44 its can be seen that the conversion using the two-phase feedstock reaches approximately 98% conversion after three hours. There is an initial lag in reaction rate, shown from the first two data points. This may be attributed to a couple factors. First is the time it takes to heat up to a reaction temperature; after only 20 minutes in the oven the solution just reaches 135°C. Another reason for this "S" type behavior may be due to the initial three phase—catalyst, oil, methanol—structure that must be overcome.

Comparing Figure 44 to the Figure 37, the reaction equilibrium can be compared. In Figure 37 (180 SSV reaction), the reaction used the one-phase feedstock (1:1:1; SBO: FFA: MeOH), seems to reach equilibrium at just under 80% after four hours, compared to the two-phase feedstock which reaches equilibrium of about 98% after three hours. So, the reaction using the one-phase solution is not as fast to reach equilibrium, by one hour, and it does not reach as high equilibrium as when using the two-phase solution in the stainless steel reactor. This is due to the fact there is less methanol available to react with in the system.

Comparing Figures 37 and 38 to Figure 38 and 40 (reaction temperature of 180°C vs 65°C) a significant difference can be observed. If we look at the equilibrium the hotter temperature has a better conversion. La Chatelier's Principle states that as pressure increases in the system, a higher temperature in this case, the equilibrium shifts toward the products. This is why the equilibrium conversion is lower at 65°C than at 180°C.

5.2.2 Effect of Co-Solvent with Respect to Initial Conversion Rates

The initial conversion rates of the two feedstocks were compared in the stainless steel vials. Like in the stirred tank reactors, the single phase feedstock increased the initial conversion rates. The data are seen in Figure 45.

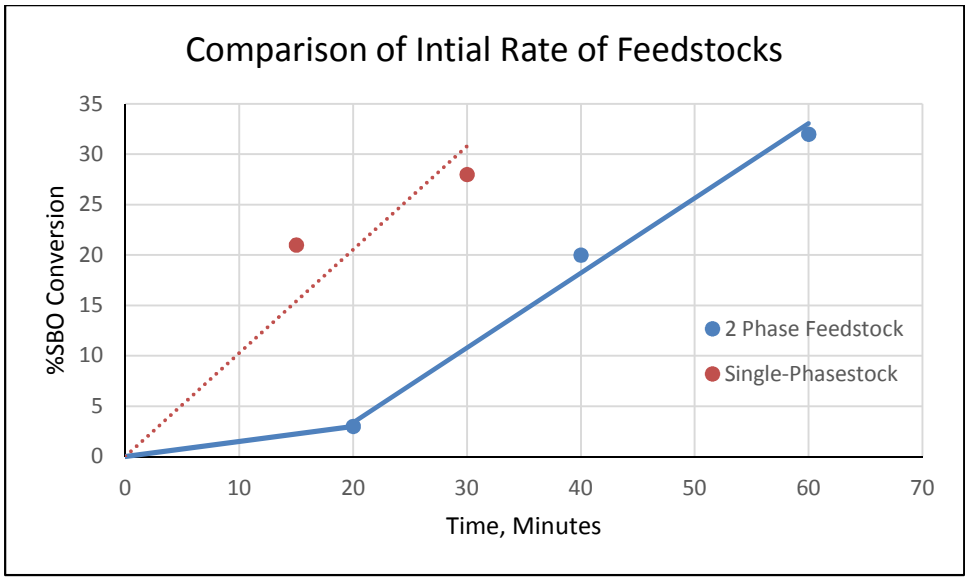

Figure 45 Comparison of Initial Rate of Feedstock in Stainless Steel Vials at 180°C

5.3 Microreactors

The microreactors used have successfully converted soybean oil into FAME in a short amount of time. The microreactor was able to achieve a conversion similar to an industrial process in less than 4 minutes. The data taken by Snider achieved the best results; this was when the microreactors were newly manufactured.

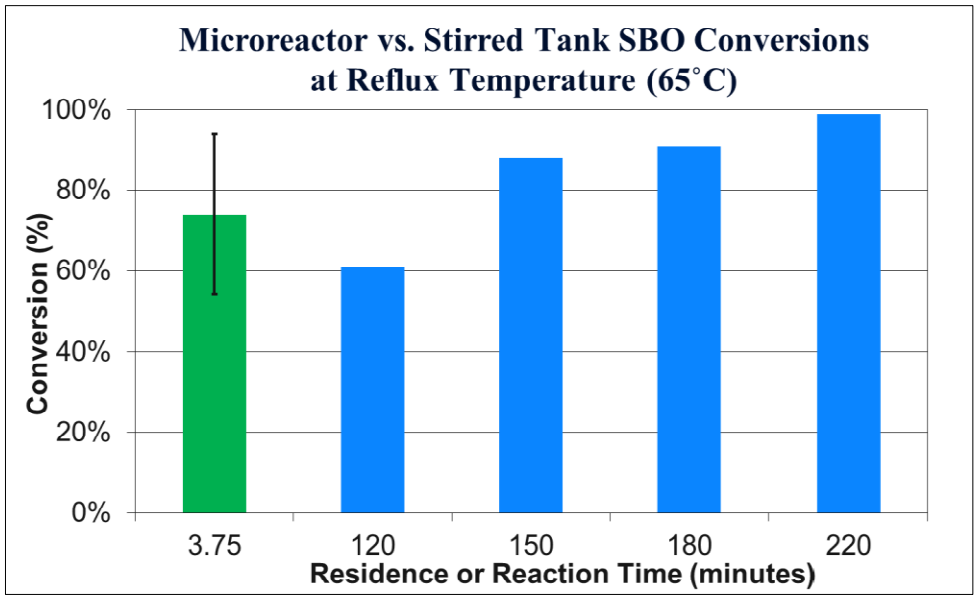

Figure 46 Comparison of Microreactor (Green) and Stirred-tank (Blue) Soybean Oil Conversion[6]

Figure 45 shows the best available comparison for conversion of SBO in microreactors. The microreactor was able to achieve a soybean oil conversion of approximately 75% with a residence time of 3.75 minutes with the 1:1 (SBO: MeOH) solution. This is significantly faster than any other method studied by this research group or in the literature. Snider also studied the conversion of pure free fatty acid with a result of approximately 17%

The conditions to achieve these conversions can be optimized further. Now only three sides of the microreactor is coated with the nickel oxide catalyst. In order for the reaction to take place all three molecules must be in contact. The main limiting factor for this to occur is diffusion time which is given by Equation 1.

$$t_D = \frac{L^2}{D} \tag{1}$$

In Equation 1, t_D represents the time it takes for an individual particle to diffuse through the liquid to the catalyst covered surface, L is the length the particle must travel, and D a diffusion coefficient. The diffusion coefficient is 1 x 10^{-9} m^2/s.[7] Right now, only the bottom and the side walls are sputtered with nickel oxide catalyst. The longest length a particle has to diffuse to react is from the top to the bottom, 50 µm. But if the top was sputtered also, the longest length a particle would have to diffuse to react is 25 µm. Thus the diffusing time would be quartered.

The same reactors that Snider used are the same reactors that were used in this study. However, the results were significantly different. There could be several reasons for this. The reactors have been stored at ambient conditions open to the air. The air may have had a catalytic poisoning effect. Also the design of the reactors required the plumbing ports be attached via adhesive. It was discovered that Superglue worked the best to adhere the ports to the microreactor. However, if not careful, the glue would seep into the inlets and clog the system. The recommended solvent to dissolve Superglue is acetone. At the beginning of the studies in 2014, all of the reactors were clogged. So to clear the channels acetone was used, with some success. However, acetone seemed to be a catalytic poison.

It is expected that the one-phase feedstock will result in a lower conversion due to the availability of methanol, compared to the one-phase feedstock. However, it is expected to be higher than the reported data, which suggests time or acetone played a part in deterioration of the microreactors. It is unclear whether time or acetone was the culprit in poisoning the nickel oxide that was sputtered on the microreactor walls, it is evident that the microreactors do not have the same activity as when they were first manufactured. The highest yield achieved in this study, 2014, was 29% soybean oil conversion. This is significantly less than the 75% soybean oil conversion immediately after manufacturing the microreactors in 2012.

5.3.1 Suggestions for Improvement

As with any design process, there are improvements that can be made for the next generation of microreactors. The specific improvements are to the reactor, not the channel design. The main operational problem is the plumbing. Leaks occur frequently and blockages occur when the plumbing adhesive seeps into the inlet ports. The top is glass and the bottom is a silicon wafer. So for the next generation of reactors, it is suggested that the inlets and outlets be part of the reactor itself. The reactor could have screw type ports so that the lines are a direct connect, thus eliminating the need for adhesive.

Another suggestion is to replace the glass with the same material as the bottom, currently silicon. That way, the top of the channel could be sputtered with catalyst and higher yields could results. Diffusion is the main source of particle mixing with a creeping flow system.[36] So having sputtering on the top would decrease the time of diffusion significantly. Having an opaque top has a drawback of not being able to see the channel. This is important because if the temperature it too high then bubbles form in the system. There is not a way to get an accurate temperature inside of the channel. This visual check helps to determine optimal operational temperature. But with proper care the solid top may prove to be a larger asset than hindrance.

CHAPTER 6

CONCLUSION

It has been shown that the 1:1:1 (SBO: FFA: MeOH) by volume feedstock will react successfully with nickel oxide, with both the soybean oil and the free fatty acid converting to biodiesel. The percent conversion of soybean oil may not be as high as with the two phase system (1:1 volume ratio of SBO:MeOH) but this could be due to higher competitiveness with the methanol.

The initial rates of conversion are increased by using the single phase feedstock as compared to the two phase feedstock. This is due to a phase boundary being eliminated, which helps the reaction proceed quicker. The single phase feedstock also had a lower equilibrium conversion was reached compared to the two phase feedstock. This is due the lower availability of the methanol in the feedstock.

The microreactors have been either clogged or have been catalytically poisoned. Due to this fact, little data were collect with them. When the microreactors were new, they performed exceptionally. With a better design for the microreactors higher conversion will be obtained.

REFERENCES

1. *Biofuels The Original Car Fuel*. 2015 [cited 2015 February 19]; Available from: http://environment.nationalgeographic.com/environment/global-warming/biofuel-profile/http://environment.nationalgeographic.com/environment/global-warming/biofuel-profile/.

2. Tanawannapong, Y., A. Kaewchada, and A. Jaree, *Biodiesel production from waste cooking oil in a microtube reactor.* JIEC Journal of Industrial and Engineering Chemistry, 2013. **19**(1): p. 37-41.

3. Canter, N., *Making Biodiesel in a microreactor.* Tribology and Lubrication Technology, 2006. **62**(8): p. 15-17.

4. Lewis, J., *Design Studies of Heterogeneous Catalysis in Microchannels*. 2010, The University of Tennessee at Chattanooga.

5. Dacus, R., *A Kinetic Study of the Production of Biodiesel Fuel from Algae Oil*. 2010, The University of Tennessee at Chattanooga.

6. Snider, E., *Catalyst Studies with Implication on the Design and Fabrication of Microreactors*. 2012, The University of Tennessee at Chattanooga.

7. Kegley, B., *The Effect of Co-Solvent and Ordered Latice Structure on Catalysis of Biodiesel Production in Microreactors*. 2014, The University of Tenneessee at Chattanooga.

8. *9-Octadecenoic Acid (Z)-Methyl Ester*. 2014.

9. *Hexadecane*. 2014; Available from: http://pubchem.ncbi.nlm.nih.gov/compound/hexadecane.

10. *Nonpetroleum Based Fuels - Bidiesel and Use Guide*. Available from: http://www.nrel.gov/vehiclesandfuels/pdfs/42672.pdf.

11. H. Bhatti, et al., *Acid and Base Catalyzed Transesterification of Animal Fats to Biodiesel.* Iran Journal of Chemical Engineering, 2008. **27**(4): p. 41-49.

12. *Catalyst Definition*. 2015 [cited 2015 February].

13. R. Richard, et al., *On-line monitoring of the transesterification reaction carried out in microreactors using near infrared spectroscopy.* Fuel, 2013. **104**: p. 318-325.

14. Guan, G., et al., *Transesterification of sunflower oil with methanol in a microtube reactor.* Ind. Eng. Chem. Res. Industrial and Engineering Chemistry Research, 2009. **48**(3): p. 1357-1363.

15. Guan, G., et al., *Two-phase flow behavior in microtube reactors during biodiesel production from waste cooking oil.* AIC AIChE Journal, 2010. **56**(5): p. 1383-1390.

16. Sun, J., et al., *Synthesis of biodiesel in capillary microreactors.* Ind. Eng. Chem. Res. Industrial and Engineering Chemistry Research, 2008. **47**(5): p. 1398-1403.

17. Kalu, E.E., K.S. Chen, and T. Gedris, *Continuous-flow biodiesel production using slit-channel reactors.* BITE Bioresource Technology, 2011. **102**(6): p. 4456-4461.

18. E. Kalu, K.C., T. Gedris, *Continuous-flow biodiesel production using slit-channel reactors.* BIoresource Technology, 2011. **102**: p. 4456-4461.

19. Wen, Z., et al., *Intensification of biodiesel synthesis using zigzag micro-channel reactors.* Bioresource technology, 2009. **100**(12): p. 3054-60.

20. Z. Wen, X.Y., S. Tu, J. Yan, E. Dahlquist., *Intensification fo biodiesel synthesis using zigzag micro-channel reactors.* Bioresource Technology, 2009. **100**: p. 3054-3060.

21. Tianming Xie, Lixiong Zhang, and N. Xu, *Biodiesel synthesis in microreactors.* Green Process Synthesis, 2012: p. 61-70.

22. Colucci, J., E. Borrero, and F. Alape, *Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing.* Journal of the American Oil Chemists' Society, 2005. **82**(7): p. 525-530.

23. *Organic Chemistry Portal*. [cited 2014 November 18]; Available from: http://www.organic-chemistry.org/namedreactions/fischeresterification.shtm.

24. Thiebaud-Roux, S., R. Richard, and L. Prat, *Modelling the kinetics of transesterification reaction of sunflower oil with ethanol in microreactors.* Chemical Engineering Science, 2013. **87**: p. 258-269.

25. Trentin, C.M., et al., *Continuous catalyst-free production of fatty acid ethyl esters from soybean oil in microtube reactor using supercritical carbon dioxide as co-solvent.* The Journal of Supercritical Fluids The Journal of Supercritical Fluids, 2011. **56**(3): p. 283-291.

26. Trentin, C.M., et al., *Continuous production of soybean biodiesel with compressed ethanol in a microtube reactor using carbon dioxide as co-solvent.* Fuel Processing Technology, 2011. **92**(5).

27. *MWV: Tall Oil Fatty Acids*. 2014 [cited 2014 January]; Available from: http://www.meadwestvaco.com/SpecialtyChemicals/PineChemicals/MWV0 02127.

28. *Methanol*. 2014 [cited 2014 January]; Available from: http://www.fishersci.com.

29. *GIlmont Falling Ball Viscometer* 2013 [cited 2015 February]; Available from: http://www.coleparmer.com/Category/Gilmont_Falling_Ball_Viscometer/7137.

30. *25 mL Round Bottom FLask*. [cited 2014 January]; Available from: http://www.sigmaaldrich.com/catalog/product/aldrich/z100641?lang=en&re gion=US.

31. *EchoTherm Programmable Hot Plate*.

32. *Reflux Condenser*. [cited 2014 January]; Available from: http://www.sigmaaldrich.com/catalog/product/aldrich/z568953?lang=en&re gion=US.

33. *5 mL Mixing Jar*. [cited 2014 January]; Available from: https://www.globalgilson.com/productdisplay.asp?model=RTA-52.

34. *20GC Gravity Convection Oven*. [cited 2014 January]; Available from: http://www.labdepotinc.com/Product_Details~id~779~pid~13532.aspx.

35. *Hermle Compact Variable-speed Universal Centrifuge - 115V; 50/60 Hz*.

36. *Creeping FLow*. Available from: http://www.engineering.uiowa.edu.

37. *n-Heptane*. [cited 2014 January]; Available from: http://www.sigmaaldrich.com/catalog/product/sial/34873?lang=en&region= US.

38. *Tricaprin*. [cited 2014 January]; Available from: http://www.sigmaaldrich.com/catalog/product/sigma/t7517?lang=en&region =US.

39. *Pyridine*. [cited 2014 January]; Available from: http://www.sigmaaldrich.com/catalog/product/sial/270970?lang=en&region =US.

40. *MXT-Biodiesel TG Column*. [cited 2014 October]; Available from: http://www.restek.com/catalog/view/7715.

41. *ASTM D6584 - 10ae1*. Standard Test Method for Determination of Toatl Monoglyceride, Total Diglyceride, Total Triglyceride, and Free and Total Glycerin in B 100 Biodiesel Methyl Esters by Gas Chromatography]. Available from: www.astm.org.

42. Baig, A. and F.T.T. Ng, *A Single-Step Solid Acid-Catalyzed Process for the Production of Biodiesel from High Free Fatty Acid Feedstocks.* ENERGY AND FUELS, 2010. **24**(5): p. 4712-4720.

43. *MSTFA- N-methyl-N-(trimethylsilyl) trifluoroacetamide*. 2014 [cited 2014 October]; Available from: http://www.sigmaaldrich.com/catalog/product/sigma/m7891?lang=en&region=US.
44. *Derivatization Reagent: Silylation*. [cited 2014 January]; Available from: http://www.sigmaaldrich.com/analytical-chromatography/analyticalreagents/derivatization-reagents/silylation.html.

45. *ASTM Standard D974*. 2008; Standard Test Method for Acid and Base Number by Color-Indicator Titration]. Available from: www.astm.org.

46. Baig, A. and F.T.T. Ng, *Determination of acid number of biodiesel and biodiesel blends.* JAOCS J Am Oil Chem Soc JAOCS, Journal of the American Oil Chemists' Society, 2011. **88**(2): p. 243-253.

47. *2-proanol (Iso-Propanol)*. [cited 2014 Januarty]; Available from: http://www.sigmaaldrich.com/catalog/product/sial/278475?lang=en&region

48. *Toluene*. [cited 2014 January]; Available from: http://www.sigmaaldrich.com/catalog/product/sial/244511?lang=en&region =US.

49. *α-Naphtholbenzein*. [cited 2014 January]; Available from: http://www.sigmaaldrich.com/catalog/product/fluka/70480?lang=en&region =US.

50. R. W. McDonald, A. T. Pritchard, and P. J, *Indroduction to Fluid Mechanics*. 2004: John Wiley and Sons.

51. *Le Chatelier's Principle*. [cited 2015 February]; Available from: http://www.chemguide.co.uk/physical/equilibria/lechatelier.html.

52. Park, J.-Y., et al., *Fast Biodiesel Production with One-Phase Reaction.* Applied Biochemistry and Biotechnology, 2009. **154**(1-3): p. 1-3.

VITA

Matthew Littell was born in Portland, Tennessee, USA to his parents Michael and Rhonda Littell. He has two older brothers named Adam and Kyle. His family is a huge support and gave him a desire for the pursuit of knowledge. Upon graduation from high school in Portland, TN Matthew moved to Collegedale, TN to attend Southern Adventist University where he obtained a Bachelor's of Science Degree in Chemistry with an Emphasis in Biochemistry. He continued his education at the University of Tennessee at Chattanooga to pursue a Master's Degree in Engineering: Chemical Sciences. While at UTC, he was a graduate assistant for the Chemical Engineering Department. There he worked with Frank Jones on biodiesel production with heterogeneous catalysis. He graduated from UTC in May 2015.